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The Manufacture and Use of Selected Inorganic Cyanides. Task III

Midwest Research Inst.

Prepared For
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April 2, 1976

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THE MANUFACTURE AND USE OF SELECTED INORGANIC CYANIDES

TASK III

JANUARY 15, 1976

FINAL REPORT

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The purposes of the study were to identify the production methods, importation, exportation, use patterns, and exposure to man and the environment of selected inorganic cyanides, including hydrogen cyanide, from 1965 to 1975. Data for the production methods included the specific process, raw materials, annual production quantities, major manufacturers, waste products, environmental management of process wastes, and other production data. Use patterns were identified and annual consumption data were compiled for each compound in the respective area of utilization. Major consumers in each use area were identified. Various possible methods for the exposure of man and the environment to inorganic cyanides were discussed and evaluated. Future production quantities and areas of usage were estimated to 1985.

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STUDY ON CHEMICAL SUBSTANCES FROM INFORMATION CONCERNING THE MANUFACTURE, DISTRIBUTION, USE, DISPOSAL, ALTERNATIVES, AND MAGNITUDE OF EXPOSURE TO THE ENVIRONMENT AND MAN

Task III - The Manufacture and Use of Selected Inorganic Cyanides

by

Ralph R. Wilkinson
Gary R. Cooper

FINAL REPORT
April 2, 1976

EPA Contract No. 68-01-2687
MRI Project No. 3955-C

For

Environmental Protection Agency
Office of Toxic Substances
4th and M Streets, S.W.
Washington, D.C. 20460

NOTICE

This report has been reviewed by the Office of Toxic Substances, Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency. Mention of tradenames or commercial products is for purposes of clarity only and does not constitute endorsement or recommendation for use.

PREFACE

This report presents the results of Task III of a project entitled "Study on Chemical Substances From Information Concerning the Manufacturing, Distribution, Uses, Disposal, Alternatives, and Magnitude of Exposure to the Environment and Man," performed by Midwest Research Institute under Contract No. 68-01-2687 for the Office of Toxic Substances of the U.S. Environmental Protection Agency. Mr. Thomas E. Kopp has been the project officer for the Environmental Protection Agency. This program had Midwest Research Institute Project No. 3955-C.

Task III, "The Manufacture and Use of Selected Inorganic Cyanides," was conducted from June 13 to November 14, 1975, by Dr. Ralph R. Wilkinson, Associate Chemist, who served as task leader, and Mr. Gary R. Cooper, Assistant Chemist. Dr. Thomas W. Lapp has served as project leader on this contract under the supervision of Dr. E. W. Lawless, Head, Technology Assessment Section. The following individuals were consultants on this task: Professor Roger Clifford, Department of Metallurgical Engineering, University of Missouri, Rolla; Dr. Leslie Lancy, Lancy Laboratories Division, Dart Industries, Inc., Zelienople, Pennsylvania; and Mr. Gerald Alletag, President, Alta Chemical Company, San Diego, California.

Midwest Research Institute expresses its sincere appreciation to the many companies who provided technical information for this report.

Results of Task I of this project, "Manufacture and Use of Selected Aryl and Alkyl Aryl Phosphate Esters," and Task II, "Production and Utilization of Selected Alkyltin Compounds," are presented in separate reports.

Approved for:

MIDWEST RESEARCH INSTITUTE

L. J. Shannon

L. J. Shannon, Assistant Director
Physical Sciences Division

April 2, 1976

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CHAPTER I

INTRODUCTION

Inorganic cyanides are widely used in industry because of their unique chemical properties. Industrial uses include:

- Metal finishing - stripping and electroplating
- Pigments for paints, inks, carbon paper, and plastics
- Mining - flotation and extraction of ores
- Metal heat treatment and case hardening
- Photographic processing
- Anti-caking agent
- Agriculture and pest control.

In addition, hydrogen cyanide is present during coking, smelting, and blast furnace operations.

CYANIDE STABILITY

Generally speaking, inorganic cyanides are not contained in consumer and household products, but are confined to the industrial, mining, and agricultural sectors because of the extreme toxicity of hydrogen cyanide gas, HCN, and the cyanide ion, CN^-. Two exceptions are photo processing chemicals and pigments which contain ferrocyanide, $Fe(CN)_6^{-4}$, and/or ferricyanide, $Fe(CN)_6^{-3}$. Cyanide in this form is not particularly toxic nor hazardous to handle because of the great stability of the iron cyanide radical ion toward dissociation and oxidation-reduction reactions. However, some experimental data indicate that even the iron cyanide radical ion can, under certain conditions, slowly release cyanide ion.

CHEMICAL CLASSES

Inorganic cyanides are primarily ionic compounds consisting of a metal cation associated with one or more cyanide radicals, e.g., sodium cyanide, NaCN, and zinc cyanide, $Zn(CN)_2$. Special cases are the complex iron cyanide radical ions previously mentioned and double salts such as $NaCu(CN)_2$. To this inorganic listing, gaseous hydrogen cyanide, HCN (or hydrocyanic acid), must be added, since it serves as a starting point in the synthesis of many other metal cyanides. Hydrogen cyanide is essentially a covalent compound in contrast to the above ionic cyanides.

Organic cyanides are largely covalent compounds and are liquids or solids and are called nitriles. The cyanide grouping, CN, is attached to a hydrocarbon or other complex grouping having a skeleton or backbone of carbon atoms. The simplest nitrile is acetonitrile, CH_3CN (also known as methyl cyanide or cyanomethane).

Nitriles are generally less toxic than inorganic cyanides, and are extensively used in the synthesis of other organic compounds, e.g., dyes, drugs, synthetic fibers, plastics, etc. Organic cyanides lie outside the scope of this report. The term cyanide will be used throughout the body of the report and will refer to inorganic cyanides only. Cyanides selected for study on this task are:

- Hydrogen cyanide, HCN
- Sodium cyanide, NaCN
- Potassium cyanide, KCN
- Calcium cyanide, $Ca(CN)_2$
- Sodium and potassium ferrocyanide
- Sodium and potassium ferricyanide
- Iron Blue (ferric ammonium ferrocyanide)
- Heavy metal cyanides as cadmium, copper, gold, silver, and zinc

OBJECTIVES AND REPORT ORGANIZATION

The primary objectives of this study are to collect information on the production quantities, manufacturers and their processes, formulators and their products, users and their processes, alternatives to cyanide materials, the environmental management of cyanide-containing effluents, and the magnitude of exposure to the environment and man.

This information is organized into a format which will assist the governmental agencies in the evaluation of any regulatory alternatives for these materials. The goal of Task III of the study has been to assist the Environmental Protection Agency (EPA) in the evaluation of the potential for environmental contamination by cyanides.

The report is organized into 10 chapters and two appendices. The Summary and Conclusions and Recommendations chapters are given early in the body of the report to allow an immediate overview. References are given at the end of each chapter for convenience. Chapter contents are as follows:

Chapter I - Introduction: Overview of industrial cyanide uses, chemical classes, specific cyanides selected, objectives of present study.

Chapter II - Summary: Degree to which objectives were met, production data of specific cyanides, manufacturing processes and waste management, usage patterns as percentage of total merchant cyanide, future trends in usage, environmental burden.

Chapter III - Conclusions and Recommendations.

Chapter IV - Historical Development and Future Outlook of Cyanides: Manufacturing processes, economic growth from 1965 to 1975, industrial future of cyanides to 1985.

Chapter V - Market Input/Output Data: Identification of cyanide manufacturers, cumulative data regarding production, importation, exportation, and capital value, usage patterns by production quantity, final products and disposal of cyanides.

Chapter VI - Manufacturing Processes: Hydrogen cyanide by Andrussow and SOHIO acrylonitrile processes, manufacturers by capacity and site, other cyanide manufacturing processes, waste disposal, transportation rates and regulations.

Chapter VII - Areas of Utilization: Metal finishing, pigment, mining operations, metal heat treatment, photography, anti-caking agents, agriculture and pest control, waste disposal, economic considerations, future growth patterns.

Chapter VIII - Cyanide Treatment Methodologies: Destruction and recovery techniques, engineering methodologies, comparison of treatment costs.

Chapter IX - Alternative Materials, Processes, and Use: Alternate raw materials and processes for cyanide synthesis, alternatives to cyanides by industrial sector.

Chapter X - Material and Energy Balance and Environmental Exposure: Raw materials, energy balance, plant capital investment, process waste material, material balance by industrial sector, estimated environmental burden by industrial sector from 1950 to 1985.

Appendix A - Thermally Generated Cyanide Sources: Coke production, blast furnace operations, estimated hydrogen cyanide production as by-product.

Appendix B - Results of Written Questionnaire.

CHAPTER II

SUMMARY

The primary objectives of this project were to collect information on environmental aspects of U.S. production and use of inorganic cyanides, alternatives to cyanides, environmental management, and exposure to the environment and man. The information was to be organized and presented in a form which will assist the EPA in assessing environmental impacts of inorganic cyanide.

The present study accomplished all the objectives and in particular indicates which cyanides are being phased out by industry and which may have continuing use in the next 10 years. The environmental impact of these cyanides is assessed.

Information acquisition and evaluation activities were designed to identify proven or potential sources of cyanides and the environmental effects of these substances. The commercially important cyanides were identified through manufacturers, formulators, distributors, users, and surveys of technical literature. The cyanides include:

* Hydrogen cyanide

* Sodium and potassium cyanide

* Calcium cyanide

* Sodium and potassium ferrocyanide

* Sodium and potassium ferricyanide

* Iron blue (ferric ammonium ferrocyanide)

* Heavy metal cyanides, including cyanides of cadmium, copper, gold, silver, and zinc

The scope of the study for each of these chemicals included identification of production sites and quantities, descriptions of manufacturing processes and environmental aspects, description of waste disposal methods, and identification of commercial uses for these products.

Sources of the project team's information included several standard and reference publications, technical literature for the chemical process industry, telephone and letter inquiries to producers, trade organizations, government agencies, formulators, distributors, users, and a written questionnaire submitted to the seven producers of hydrogen cyanide.

The major findings in this study are briefly described in the following subsections.

MERCHANT CYANIDE PRODUCTION QUANTITIES, SITES AND MANUFACTURERS

Production data for the 14 cyanides of interest are presented in Table 1.

The production rates, sites, and manufacturers range from two manufacturers of gold cyanide in New Jersey at 200,000 lb annually to seven manufacturers of hydrogen cyanide at 375 million pounds annually. Production sites of hydrogen cyanide are located in Texas (3), Louisiana, Tennessee, Ohio, and New York State.

Sodium cyanide is the next most prominent cyanide with a production of about 56.5 million pounds annually. Other cyanides are manufactured in relatively small quantities and are derived from either hydrogen cyanide or sodium cyanide. Total metal cyanide production is 79.2 million pounds. The total of all cyanides is 454.2 million pounds.

Emphasis is placed on the quantity of cyanides produced for merchant sales in contrast to cyanides produced for captive use. Statistical data are more generally available for merchant trade cyanides and are considered proprietary information when applied to captive cyanides. Thus, a reasonably accurate estimate (5 to 10%) of merchant trade cyanides can be given but essentially no production information is available for cyanides used internally.

Captive cyanides are used as raw materials in the production of other materials. For example, sodium cyanide is captively consumed in the manufacture of chelating agents, EDTA and NTA, but no production figures are available for these purposes. Adiponitrile is now principally manufactured via cyclohexane and adipic acid and no longer requires hydrogen or sodium cyanide.

Potassium cyanide is captively consumed in the manufacture of cyanogen gas and malonic acid. Cyanogen is an intermediate for medicinals, photographic chemicals, and military poison gas. Malonic acid is an intermediate

Table 1. MERCHANT CYANIDE PRODUCTION, QUANTITIES, SITES AND MANUFACTURERS IN 1975

Cyanide[a]	Total production[b] (10^6 lb/year)	Production sites in U.S.	Number of manufacturers
Hydrogen cyanide	375.0	7	7
Sodium cyanide	56.5	1	1
Calcium cyanide[c]	-	-	-
Iron blue	8.0	3	3
Zinc cyanide	7.0	2	2
Sodium and potassium ferrocyanides	2.5	3	3
Potassium cyanide	2.0	2	2
Copper cyanide and sodium and potassium copper double salts	1.5	1	1
Cadmium cyanide	0.6	1	1
Silver cyanide	0.5	2	2
Sodium and potassium ferricyanides	0.4	2	2
Potassium gold cyanide[d]	0.2	1	1
Total	454.2		

---

[a] The cyanides are listed in descending order of total production.

[b] Midwest Research Institute (MRI) estimated 1975 production.

[c] There are no domestic producers of calcium cyanide. Imports amounted to 8.0 million pounds in 1975.

[d] *Chemical Week*, p. 23, April 23, 1975.

for polymethine dyes, synthetic caffeine, and medicinals. No production figures for potassium cyanide for these purposes are available.

Calcium cyanide is captively consumed for organic synthesis and for production of heavy metal cyanides, including ferro- and ferricyanides, and iron blue.

MANUFACTURING PROCESSES THAT PRODUCE CYANIDES

Hydrogen cyanide is produced as a primary product by the Andrussow process. It is estimated that 275 million pounds are produced in this manner. A second process, SOHIO-acrylonitrile, yields hydrogen cyanide as a by-product. It is estimated that 200 million pounds are produced by this process but that 100 million pounds are incinerated. Of the total 375 million pounds available for use, only about 11% enters the inorganic sector, principally as sodium cyanide, and the remainder is used for organic synthetic purposes.

Other cyanides are manufactured by simple replacement and/or oxidation-reduction reactions. Hydrogen cyanide is also produced as an unwanted by-product from coke ovens and blast furnaces. There are approximately 60 million pounds of hydrogen cyanide generated by coke ovens annually. Coke oven gases are used in blast furnaces as an additional fuel.

WASTE MANAGEMENT

The wastes produced by the various manufacturing processes generally involve solids as complex iron cyanides and are handled by landfill or by deep well injection. Liquid wastes occurring as cyanide liquors and nitriles are generally treated by alkaline chlorination. Waste gases as hydrogen cyanide and as volatile nitriles are incinerated.

INDUSTRIAL USAGE PATTERNS OF CYANIDES

The usage patterns of industrial cyanides are given in Figure 1. Metal finishing operations including cleaning, stripping, plating, bath makeup, and maintenance account for about 62.5% of total merchant cyanide as NaCN equivalent. Principally, sodium cyanide is employed but heavy metal cyanides, especially zinc cyanide, are important. Iron blue (ferric ammonium ferrocyanide) is an important article of commerce and accounts for 16.9% of cyanide consumption as pigment. All other sectors account for less than 10% each.

FUTURE TRENDS IN CYANIDE USAGE

Substitutes for cyanides in some industrial processes are being sought and utilized. Specifically, it is forecast that metal finishing usage of sodium and heavy metal cyanides will decrease by at least 25% over the next 10 years as noncyanide plating baths, especially zinc baths, are developed. The same trend is noted in metal heat treatment as noncyanide liquid baths and gaseous processes involving methane and/or ammonia are developed.

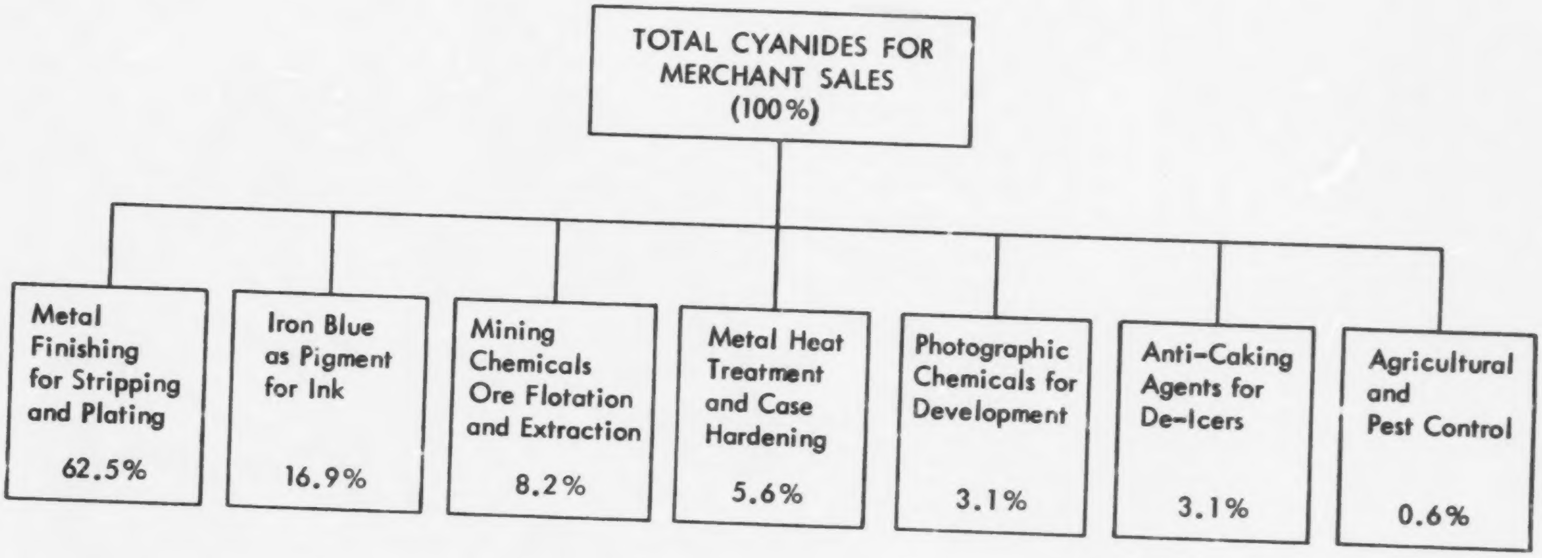

TOTAL CYANIDES FOR MERCHANT SALES (100%)
Metal Finishing for Stripping and Plating 62.5%
Iron Blue as Pigment for Ink 16.9%
Mining Chemicals Ore Flotation and Extraction 8.2%
Metal Heat Treatment and Case Hardening 5.6%
Photographic Chemicals for Development 3.1%
Anti-Caking Agents for De-Icers 3.1%
Agricultural and Pest Control 0.6%

Figure 1. Industrial patterns of cyanides as percentages of merchant sales (NaCN equivalent)

Photographic chemicals using ferro- and ferricyanides are declining as systems based on ferric ion and EDTA become more prominent. Agricultural uses of cyanides as fumigants and insecticides and for pest control as rodenticides are no longer economically significant.

A continued usage of cyanides as iron blue for pigment in inks, carbon paper, as a plastics colorant and for industrial paints is forecast. Likewise, mining applications for ore flotation and extraction, principally as sodium cyanide, and anti-caking agents for de-icers, principally as ferrocyanide and iron blue, continue to consume a small but significant quantity of cyanide.

ENVIRONMENTAL BURDEN OF CYANIDES

Practically all industrial cyanide is handled by one or more waste treatment processes to yield cyanate or carbon dioxide and nitrogen and heavy metal hydrated oxides. Cyanides as ferrocyanide and iron blue are dispersed in runoff waters, along highways from de-icing operations and may eventually be degraded and oxidized by sunlight, heat and normal weathering conditions. Much cyanide as iron blue is disposed by landfill operations. The fate of iron blue in anaerobic condition in the absence of light and heat is unknown at present. If the anaerobic degradation process is relatively slow, e.g., only 5% degradation per year, a significant amount of iron blue could be accumulating in the environment. Fortunately, iron blue is not toxic.

CHAPTER III

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions are drawn on the basis of this study.

1. Overcapacity for hydrogen cyanide exists at present. The needs of hydrogen cyanide could be met with existing SOHIO-acrylonitrile plants yielding by-product HCN and one or two large Andrussow process facilities.

2. Rapidly changing industrial processes and markets are causing a decrease in long-term demand for hydrogen cyanide which will likely continue for the next 10 years.

3. Metal cyanides are very prominent industrially with the two largest sectors being metal finishing (62.5%) and pigment (16.9%).

4. Chemical substitutes for cyanides are being researched and developed. If successful, these will largely replace cyanides and cause a significant drop in cyanide usage in all sectors, with the possible exceptions of mining operations, pigments and as anti-caking agents. By 1985, cyanide consumption will be 50 to 75% of its present usage, i.e., a drop to 40 to 60 million pounds from the present 80 million pounds of NaCN equivalent.

5. Over the next 10 years, a 2 to 3% growth rate is forecast for iron blue by industry sources. Consumption of cyanides by mining operations will continue at present levels over the next 10 years as will anti-caking agents usage.

6. In general, proper cyanide waste management has been observed by nearly all major cyanide users since 1970. Alkaline chlorination and landfill operations are the more prominent of several options available.

7. Very little regeneration of cyanides has been observed. One exception lies in the photographic chemicals sector where conversion of ferrocyanides to ferricyanides by persulfate oxidation or ozonation is becoming prominent. The economics are favorable for regeneration.

8. Environmental burden due to ferrocyanides and iron blue as anti-caking agents and iron blue as pigment may become prominent in the future. Fortunately these chemicals have low toxicity.

The following recommendations are offered:

1. Continue encouragement of lower cyanide waste levels in the metal finishing area through the establishment of effluent guidelines and standards of performance.

2. Continue to monitor mining waste operations and encourage good housekeeping and safety practices regarding tailings ponds.

3. Encourage research and development toward regeneration or recycling of cyanides particularly in the metal finishing and photographic sectors.

4. Encourage research and development to find economic and easily degradable blue pigments as a substitute for iron blue.

5. Encourage the development of economical and easily degradable anti-caking agents for de-icers as substitutes for ferrocyanides and iron blue.

6. Determine decomposition kinetics and mechanism for ferrocyanides and iron blue in runoff waters from highway de-icing operations.

7. Determine decomposition kinetics and mechanism for ferrocyanides and iron blue under landfill management conditions.

CHAPTER IV

HISTORICAL DEVELOPMENT AND FUTURE OUTLOOK OF CYANIDES

The historical development of cyanides for industry, mining, and agriculture is reviewed. The future outlook of cyanides from 1975 to 1985 is discussed from a generalized viewpoint.

HISTORICAL DEVELOPMENT TO 1948

Cyanides have been employed in electroplating since 1840 when special solutions for gold and silver plating were developed by Elkington. Photographic applications date from 1884 with Farmer's Reducing Solution utilizing ferro- and ferricyanides. In 1888, MacArthur and Forrest developed a gold cyanidation process and commercial extraction of low-grade gold and silver ores began the following year.

The usage of cyanides in metal finishing, i.e., stripping and electroplating operations, constitutes the largest industrial sector today. Other uses of cyanides are economically significant, e.g., metal heat treatment and case hardening and pigments, but they do not rate even a close second in overall utility of cyanides when compared to metal finishing.

Cyanide synthesis and commercial production has had a long history and has been reviewed by a number of authors.1/ In general, the historical synthetic routes extend back at least to Scherlein 1782, and have been modified by various talented individuals, culminating in two very successful processes, namely, the Castner process (1900) and the American Cyanamid process (1917).

The early routes relied on nitrogenous organic matter, ammonia, or nitrogen gas as the source of nitrogen, and the reaction with carbonates and coke was carried out at high temperatures near 900 to 1000°C in iron vessels. The products were always impure and contained traces of iron.

A very successful process by Beilby (1891) in Scotland utilized potassium and sodium carbonates, carbon and ammonia:

$$Na_2CO_3 + K_2CO_3 + 8C + 4NH_3 \longrightarrow$$
$$2NaCN + 2KCN + 6CO + 6H_2$$

The process could not be made to yield pure sodium cyanide.

World production of metal cyanides by 1897 reached 13 million pounds annually, and rose to 50 million pounds by 1915. This increased production was largely the result of the Castner process (1900) which yielded a high grade of sodium cyanide and largely displaced the more expensive potassium cyanide except for electroplating operations.

The Castner process combines metallic sodium, charcoal, and ammonia as follows:

$$2Na + 2C + 2NH_3 \longrightarrow 2NaCN + 3H_2$$

It takes place in stages involving sodamide as an intermediate. The raw materials are heated to 800°C in iron vessels, and the molten water-like cyanide can be easily cast into "eggs" containing 98% NaCN. The hydrogen can be recovered in high purity. Even as late as 1964, plants operating in England, Spain, France, and Germany were using an updated form of the Castner process.

Large quantities of alkali cyanide have been made in the U.S. by heating calcium cyanamid with coke or charcoal in electric furnaces above 1000°C to form "black" cyanide, $Ca(CN)_2$. Thus,

$$CaNCN + (\text{excess})\ C \xrightarrow[NaCl]{1100^\circ C} Ca(CN)_2$$

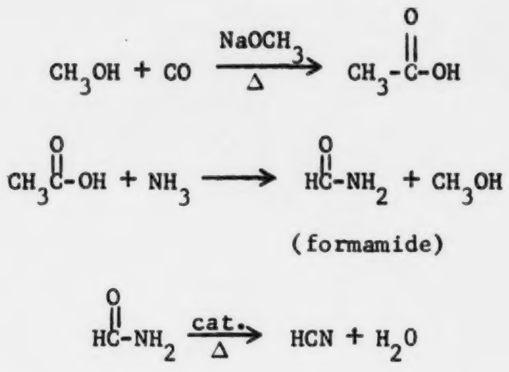
From calcium cyanide other cyanides can be made by treating it with metal carbonates. For example,

$$Ca(CN)_2 + Na_2CO_3 \longrightarrow 2NaCN + CaCO_3$$

American Cyanamid Company has been largely responsible for development of these processes starting in 1916 as a direct result of World War I. With several of these processes operating simultaneously in various parts of the world, total annual consumption of sodium cyanide reached 160 million pounds in 1963, excluding the Communist Bloc, for which consumption data are lacking.

Sodium cyanide or calcium cyanide can be utilized to form many other cyanides, including hydrogen cyanide by direct acidification, ferro- and ferricyanides, iron blue, heavy metal cyanides, and a host of organic derivatives (nitriles).

Hydrogen cyanide can also be made by catalytic dehydration of formamide (1932). Thus:



$$CH_3OH + CO \xrightarrow[\Delta]{NaOCH_3} CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH$$

$$CH_3\overset{\overset{O}{\|}}{C}\text{-}OH + NH_3 \longrightarrow H\overset{\overset{O}{\|}}{C}\text{-}NH_2 + CH_3OH$$

(formamide)

$$H\overset{\overset{O}{\|}}{C}\text{-}NH_2 \xrightarrow[\Delta]{cat.} HCN + H_2O$$

The final step requires temperatures up to 650°C with an alumina catalyst. This process was popular in Germany.

HYDROGEN CYANIDE

In 1948, the major American producers of hydrogen cyanide were E. I. du Pont de Nemours and Company and American Cyanamid Company. The combined production of hydrogen cyanide (by acidification as described above) amounted to 40 million pounds annually. Hydrogen cyanide was also obtained from coke oven gas during coking operations. In 1948, Pittsburgh Coke and Chemical Company (now Shenango Company) recovered 1 million pounds of hydrogen cyanide from coke oven gas.[2] This process also constituted a source of sodium cyanide, since HCN could be trapped in caustic and sold for electroplating and organic synthesis purposes. Recovery of cyanide from coke oven gas ceased about 1960.

However, in 1948, the synthetic route for hydrogen cyanide and metal cyanides changed dramatically with the introduction of the world's first plant for the captive production of HCN from natural gas, ammonia, and air by Rohm and Haas Company at Deer Park (Houston), Texas.[2] The principal use of the hydrogen cyanide was for the production of acetone cyanohydrin, an intermediate of methyl methacrylate. Two other companies, Carbide and Carbon Chemicals (now Union Carbide Company) and Monsanto Chemical Company soon entered the field, and by 1953 over 200 million pounds capacity of HCN was in existence.

The synthetic route involved the oxidation of ammonia in the presence of methane, and was devised by Andrussow in 1933. Thus:

$$2CH_4 + 3O_2 + 2NH_3 \xrightarrow[1000°C]{cat.} 2HCN + 6H_2O$$

Hydrogen cyanide occurs to the extent of 7% by volume in the reaction gas.[3/]

More recent adaptations of the synthetic route to HCN include the Degussa process (West Germany, 1958) which uses no air or oxygen, just ammonia and methane. The two reactants are passed through externally heated ceramic tubes containing a platinum catalyst at 1200 to 1250°C. The reaction is:

$$NH_3 + CH_4 \xrightarrow[1250°C]{cat.} HCN + 3H_2$$

This process is limited to a smaller scale than is the Andrussow process because of a lower production rate and relatively fragile equipment.

The Shawinigan Chemicals Division of Gulf Oil Canada, Ltd., developed an alternate route for the production of HCN from ammonia and propane in the absence of air using an electrothermal fluidized bed of coke at 1500°C with no catalyst. The plant operated from 1960 to 1968, and was closed for economic reasons, not technical problems. The HCN produced was transitory and converted directly to sodium cyanide.

U.S. production capacity by the Andrussow process or modifications thereof grew rapidly from 1948 to 1965 as new companies entered the field, and as older facilities expanded. Published annual capacity in 1963 was 415 million pounds, and production rose from 40 million pounds prior to the Andrussow process in 1948 to more than 450 million pounds in 1965. This figure supplied by the Bureau of Census is known to be understated since interplant transfers of HCN are not counted as consumption in producing plants. Hence, total consumption was more nearly 550 million pounds.

The principal uses for HCN from 1948 to 1960 were for plastics and organics (acrylonitrile, methyl methacrylate, adiponitrile, chelating agents, lactic acid, pharmaceuticals, alkylamines, etc.). Only a small amount of hydrogen cyanide was converted to alkali cyanides, pigments (iron blue), ferro- and ferricyanides, and heavy metal cyanides. It has been estimated that the combined market for all inorganic cyanides accounted for approximately 10 to 20% of HCN production. This estimate holds true today as well.

In 1960, Standard Oil of Ohio (SOHIO) developed a new process for acrylonitrile production which yielded HCN as a by-product. Thus, acrylonitrile, instead of being an important consumer of HCN, became an important producer of HCN. The first SOHIO-based acrylonitrile plant was placed in operation by Vistron Corporation (a subsidiary of SOHIO) in 1962 at Lima, Ohio. This plant produced 8 million pounds of HCN annually. Approximately 0.15 to 0.20 lb of HCN are produced as by-product for every pound of acrylonitrile that is produced.[3]

From 1962 to 1965 the hydrogen cyanide producers expanded their capacity, and HCN production rose from 170 to 450 million pounds (and higher if interplant transfer is counted) as demand for HCN for use in organics rose. The inorganic needs for HCN grew slowly, as no new markets were developed.

From 1965 to 1967 many of the original acrylonitrile plants using HCN as a raw material converted to the SOHIO process, causing demand and production of HCN to slide downward from the peak of 450 to 250 million pounds. Much of the by-product HCN was incinerated as demand slumped. The last HCN-based acrylonitrile plant which was operated by Monsanto at Texas City, Texas, closed in August 1970. From an estimate of nearly 80% production capacity in 1965, the industry fell to a level near 55% of production capacity in 1970.[4]

However, beginning in 1967, strong interest was shown in nitrilotriacetic acid (NTA) as a replacement for phosphate as a builder in detergents. This trend rejuvenated the HCN market, since HCN is a raw material for NTA.[5] The methyl methacrylate market began growing rapidly and production of HCN rose again to a peak near 370 million pounds (or higher) in 1969.

In 1970, Ethyl Corporation planned an 85 million pound HCN facility along the Houston Ship Channel and contracted Chemico (Chemical Construction of New York) to design the plant.[6] Ethyl Corporation planned to use HCN for manufacture of NTA. If completed, the HCN capacity would rise to near 650 million pounds.

Meanwhile, the Hampshire Division of Grace Chemical Company expanded its original 20 million pound NTA plant (1967) to 60 million pounds capacity by 1970.[4] By 1969 Monsanto was producing 75 million pounds of NTA in Alvin, Texas, and planned to expand to a 350 million pound NTA plant in Texas City, Texas. Other companies indicated an interest in NTA production, e.g., E. I. du Pont de Nemours and Company.

These very hopeful estimates of perhaps 500 million pounds annual production of NTA, with a consequent rise to perhaps 500 million pounds of HCN annually, were made in the face of an unresolved nitrate pollution potential arising from NTA degradation.[7] Thus, although NTA was considered a biodegradable product and a possible substitute for phosphates in detergents, it was also a potential cause of nitrate pollution.

In December 1970, the EPA released results of an NTA study which showed that NTA, in combination with cadmium and methyl mercury, could cause a high incidence of fetal injuries in rats and mice. The EPA recommendation was to stop using NTA pending further tests and review.

The EPA report caused Proctor and Gamble to make a clean break with NTA. The result of the report was to cause the HCN producers to drop expansion plans of more than 750 million pounds annually. The Ethyl Corporation cancelled plans for its NTA plant. The property remains vacant today. Monsanto Company halted construction of 450 million pound NTA facilities at Alvin and Texas City, Texas. W. R. Grace Company suspended plans for a 100 million pound NTA plant in Ontario, Canada.[8]

The latest information regarding hazards of NTA came from the National Cancer Institute and the National Institute of Environmental Health Sciences. Long-term studies show that NTA causes the development of urinary tract cancers in rats and mice.[9] Thus, NTA seems to offer no future markets for hydrogen cyanide.

The result of these actions has slowed HCN growth significantly to date. Since 1970, HCN production has hovered near 300 million pounds annually. Present capacity is more than adequate to handle present markets.

The most recent estimate of HCN future production is by the Chemical Marketing Reporter, December 10, 1973. This source estimates HCN growth at 5.5%/year through 1977. Growth will occur principally because of methyl methacrylates and other plastics and synthetics. Hopes for NTA revival appear nil. The inorganic cyanide market provides no growth opportunity for HCN since this market is amply supplied by current production and facilities in existence.

Finally, an opinion from T. C. Ponder, Petrochemicals Editor of Hydrocarbon Processing, is offered regarding the future of hydrogen cyanide:

> "New technology for the major consumers of hydrogen cyanide have almost killed this old standby. Never a real tonnage petrochemical, HCN is now reserved for those specialties products where its chemistry makes the reaction simple.

"However, large tonnages of HCN are produced in most industrialized areas of the world but most of this is incinerated for disposal.

"Acrylates are now made from propylene; acrylonitrile is now made from ammonia and propylene. These direct processes no longer require HCN as a raw material. Conversion to the SOHIO process throughout the world is almost completed for acrylonitrile and all new acrylonitrile plants will use this or the Ugine or Snamprogetti technology. Any new acrylic acid or ester processes will continue to use propylene directly and the melamine business has converted to urea. There just doesn't seem to be any good reason for making HCN."[10]

These erratic trends in HCN production are well illustrated in Figure 2 and are primarily due to shifts in demand for certain organic chemicals, e.g., acrylonitrile, methyl methacrylate, and NTA.[11,12]

ALKALI METAL CYANIDES[1]

The two commercially prominent alkali metal cyanides are sodium cyanide and potassium cyanide. Of these, sodium cyanide is produced and utilized to a much greater degree than potassium cyanide, perhaps by a factor of 20. Only in special applications, e.g., special electroplating baths, is potassium cyanide specified over sodium cyanide. Potassium cyanide is considerably more expensive than sodium cyanide, primarily because of the low production volume, and also because of the high cost of potash relative to soda ash. Since these two cyanides are so similar in nature, they are grouped together for discussion and they will be differentiated only if it is relevant to the discussion.

Alkali cyanide manufacture has been described earlier in connection with hydrogen cyanide. The historical methods of manufacture are no longer of significance. The modern method of preparation involves neutralization of hydrogen cyanide by NaOH or KOH solution. The process appears straightforward and simple, but this is, in fact, not the case. The resulting solution of alkali cyanide must be evaporated under reduced pressure and in a highly controlled manner to avoid loss of hydrogen cyanide through hydrolysis of the cyanide ion.

After evaporation of the cyanide solution, a fine powder is obtained which is then briquetted or fused to obtain a product conveniently handled. Purity is greater than 99%. E. I. du Pont de Nemours and Company is the principal manufacturer of sodium and potassium cyanide, and markets

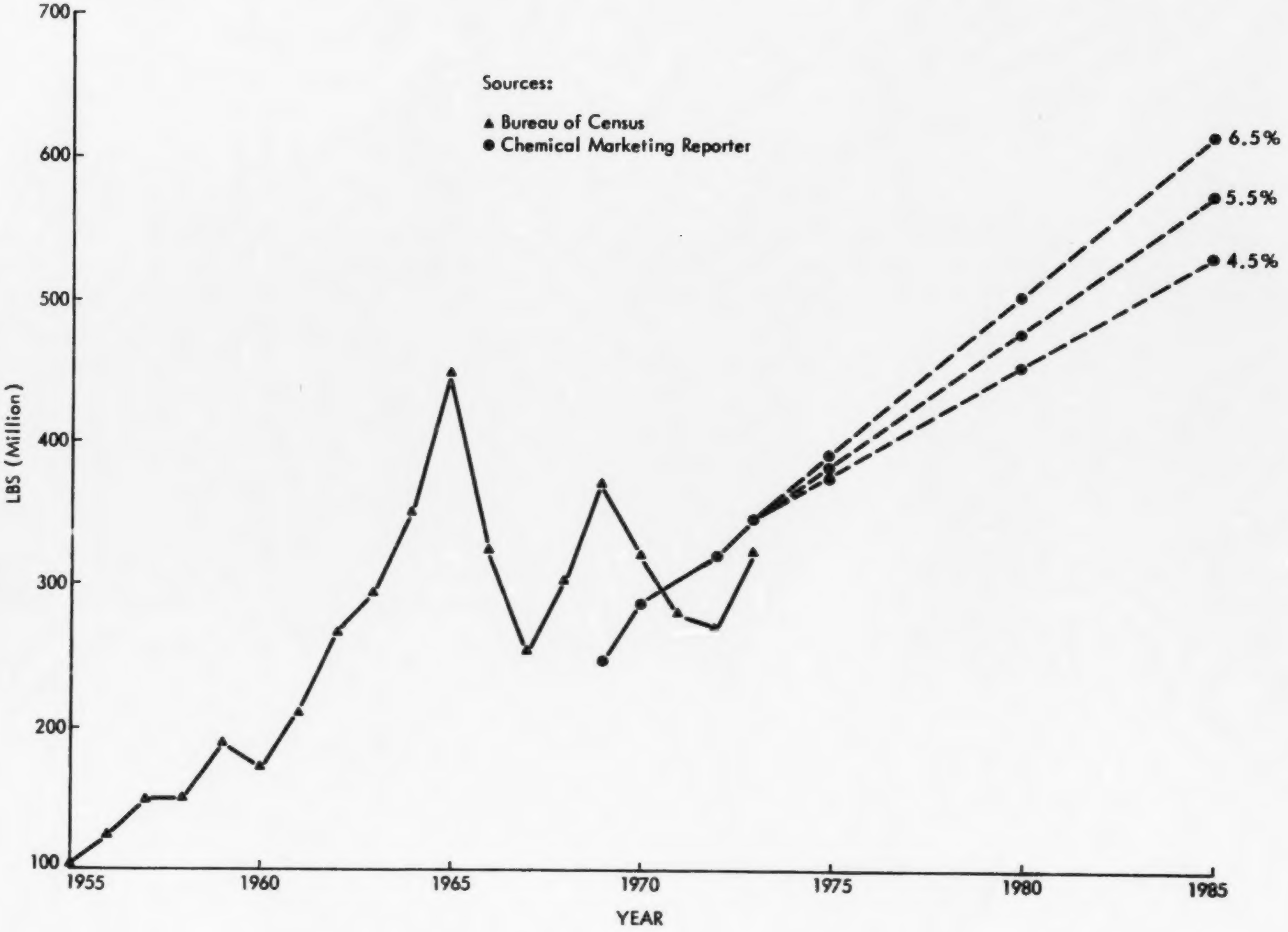


Figure 2. Domestic HCN production

these products as a briquette or in granular form. Some sodium cyanide is sold as a solution containing 30% by weight.

The historical markets for alkali cyanides have remained unchanged. Considerable amounts are used as such in mining for flotation and extraction of ores, for metal heat treating and case hardening as proprietary salt baths, for electroplating and metal stripping as proprietary baths, for the preparation of heavy metal cyanides for electroplating, for the preparation of complex metal cyanides, e.g., ferro- and ferricyanides and iron blue, for agricultural uses as pest control agents and fumigants, and in the manufacture of a host of organic cyanides (nitriles).

Commercial potassium cyanide is made in a manner similar to sodium cyanide, but is of slightly lower purity, 97 to 99%. The principal contaminants are sodium cyanide and potassium carbonate.

The principal use of potassium cyanide is in electroplating, wherein the salt has superior "throwing power" over the sodium salt; in other words, potassium cyanide electroplating solution has a higher current efficiency. Some potassium cyanide is used in conjunction with sodium cyanide for metal heat treating salts and in salt mixtures for metal coloring by chemical or electrolytic processes.

As a group, the alkali cyanides have shown little significant commercial growth other than as a result of the general expansion of the economy. No new uses of alkali cyanides are anticipated. The normal growth via expansion of the economy may be offset to some extent by the introduction of noncyanide salt baths into the metal heat treatment and electroplating sectors. Historically, a 3% growth in sodium cyanide has taken place between 1965 and 1970, and new applications for cyanides appear unlikely in the future.

ALKALINE EARTH CYANIDES[1/]

Only calcium cyanide is of any commercial importance in the class of alkaline earth cyanides. Other alkaline earth cyanides are known and have been characterized, but they offer no advantage over calcium cyanide and are much more expensive.

Calcium cyanide is generally manufactured by heating crude calcium cyanamid with carbon in an electric furnace to 1000°C in the presence of sodium chloride. The resulting melt is cooled rapidly to prevent reversal of the reaction. The crude calcium cyanide is called "black cyanide" and is sold in blocks, flakes, granules, or powder form.

Uses of calcium cyanide include fumigation wherein the powder form rapidly hydrolyzes in moist air to release hydrogen cyanide. Some calcium cyanide is used in metal heat treatment and some is sold as a 15% solution for gold extraction. Sodium or potassium ferrocyanide utilizes calcium cyanide as a starting material.

Much calcium cyanide has been imported from American Cyanamid Ltd., of Canada. However, the market for calcium cyanide has been declining rapidly since 1970, since its use in agriculture as a fumigant and pest control agent has been supplemented by other chemicals. Some proprietary salts for heat treating have been developed that do not contain calcium cyanide.

HEAVY METAL CYANIDES

This class of cyanides contains a transition metal and the cyanide radical. They can be simple compounds like copper cyanide or complex cyanides as sodium ferrocyanide, sodium ferricyanide, or ferric ammonium ferrocyanide (iron blue). The heavy metal cyanides are prepared by simple replacement reactions from a metal salt and sodium cyanide.

The commercially important heavy metal cyanides include those of copper, cadmium, gold, silver, and zinc. These are generally used in electroplating applications. Accurate marketing data are difficult to obtain since the manufacturers consider this information proprietary. However, the future market for these materials in the electroplating area is tied to the general economy; also noncyanide plating baths are becoming significant, which may lower heavy metal cyanide consumption especially in zinc plating.

The historical market for iron blue as a paint pigment has recently shifted to that of chemical coatings, printing ink, carbon paper, paper manufacture, and plastics. The market for inks and carbon paper is growing rapidly and iron blue consumption will rise and fall with the general economy.

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CHAPTER V

MARKET INPUT-OUTPUT DATA

This chapter identifies manufacturers of industrially important cyanides and presents cumulative data for the selected cyanides during the years 1965 through 1973. The data are considered in terms of production, importation, exportation, use patterns, and final disposal.

MANUFACTURERS

Table 2 lists manufacturers of industrially important cyanides in 1975. Historical changes in this select group of companies are presented in detail when dealing with a specific cyanide or classes of cyanides.

PRODUCTION AND CAPITAL VALUE

Hydrogen Cyanide

The total annual production quantities of selected cyanides for the last 10 years and for a 10-year projection from 1975 to 1985 are shown in Table 3. The table requires a number of comments in order for the reader to understand the limitations of these data. Production figures for HCN are based on Census Bureau data, which are known to be understated. Actual production of HCN was probably 25% higher in most years since interplant transfers are not counted by the Census Bureau. Further, all HCN that is produced but not isolated is not reported, e.g., direct conversion to NaCN. Some HCN is produced as a by-product of acrylonitrile manufacture and is at present being incerated. Future growth of HCN is assumed to be linear at 4.5%/year, and was adjusted downward from an estimate of 5.5%/year by the *Chemical Marketing Reporter*.[1]

A comparison of Census Bureau, Stanford Research Institute, and *Chemical Marketing Reporter* production estimates for HCN is given in Table 4.

Table 2. MANUFACTURERS OF SELECTED CYANIDES IN 1975

Company	HCN	NaCN	KCN	$Ca(CN)_2$	Ferrocyanides, ferricyanides	Iron blue	Heavy metal cyanides
American Cyanamid Company	X			X[a]		X	
C. P. Chemicals, Inc.							X
City Chemical Corporation							X
Dow Chemical Company	X						
E. I. du Pont de Nemours and Company	X	X	X				X
Engehard Industries, Inc.							X
Fisher Scientific Company		X	X		X		X
Harshaw Chemical Company						X	
Harstan Chemical Company							X
Hercules, Inc.	X				X	X	
M&T Chemicals, Inc.							X
Mallinckrodt Company			X		X		X
Monsanto Chemical Company	X						
Phillips Brothers Chemical Company							X
Rohm and Haas Chemical Company	X						
Vistron Corporation (SOHIO)	X						

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a/ Imported from Canadian affiliate.

Table 3. DOMESTIC PRODUCTION OF SELECTED CYANIDES
(million lb annually)

Year	HCN	NaCN[a]	KCN	Iron blue	Heavy metal cyanides[b]
1965	451	32.0	1.7	11.0	
1966	323	34.0	1.7	11.0	
1967	252	35.0	2.0	11.6	
1968	304	38.3	2.2	12.0	
1969	370	45.0	2.1	11.6	
1970	321	42.8	2.3	10.4	
1971	282	46.1	2.5	10.8	
1972	272	41.1	2.3	10.4	
1973	322	45.1	2.3	10.1	
1974	356	45.1	2.1	9.0	
1975	375	43.0	2.0	8.0	13
1980	453	38.0	1.7	10.3	
1985	530	32.0	1.6	11.8	

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a/ Domestic production for merchant sales but excluding exports.

b/ Including ferro- and ferricyanides.

Table 4. COMPARISON OF ESTIMATED HYDROGEN CYANIDE PRODUCTION

Year	SRI	CMR	Census Bureau
		(million lb HCN annually)	
1963	440	293	293
1964	480	-	350
1965	530	-	451
1966	450	220	323
1967	390	218	252
1968	430	-	304
1969	500	247	370
1970	-	285	321
1971	-	-	282
1972	-	320	272
1973	-	345	322

The large discrepancies between Census Bureau production data,[2] SRI estimates of consumption,[3] and CMR estimates of consumption are related to inadequate information, differences in counting methodology, possible double counting, and to the point made earlier, that HCN is sometimes produced but not isolated. This report will draw upon Census Bureau data since these data are more complete, readily available, and do not require estimates of HCN which has only a transitory existence. (The rationale behind the erratic production history for HCN has been given in Chapter IV.)

The present manufacturers of HCN are given below:

American Cyanamid Company,
Dow Chemical Company,
E. I. du Pont de Nemours and Company,
Hercules, Inc.,
Monsanto Company,
Rohm and Haas Texas, Inc., and
Vistron Corporation Division of SOHIO.

Other companies no longer producing HCN are: B. F. Goodrich Company; Union Carbide Corporation; and Ethyl Corporation which planned an HCN facility in 1970, but never built.

Table 5 presents the capital value of selected cyanides by type or grade as raw materials. Estimates of capital value for 1975 through 1985 are given, and assume a linear rise of 8% annually on prices.

Sodium Cyanide

Sodium cyanide is a prominent industrial cyanide, and a complete production, importation, and exportation history of this compound is given in this chapter. Total sodium cyanide available for merchant sales is given by domestic production plus imports. The total amount produced domestically is given by domestic merchant sales plus exports. Figure 3 illustrates these relationships and estimates these quantities for 1975.

Figure 4 presents the distribution of sodium cyanide as merchant sales in various industrial sectors in 1975. The total of 80 million pounds of NaCN equivalent was obtained by independently estimating the quantity used in each sector and summing. The overall standard deviation of this estimate is ± 6.6 million pounds, which is an 8% relative uncertainty. The principal source of uncertainty is the metal finishing sector.

Table 5. CAPITAL VALUE OF SELECTED CYANIDES - DOMESTIC PRODUCTION
(million dollars)

Year	HCN[a]	NaCN[b,e]	KCN[c]	Iron blue[d]
1965	51.9	6.23	0.72	6.16
1966	37.2	6.63	0.72	6.32
1967	29.0	6.82	0.85	6.73
1968	35.0	7.36	0.94	7.26
1969	42.6	8.65	0.89	7.26
1970	36.9	8.22	0.98	7.06
1971	32.4	8.86	1.06	6.80
1972	31.2	8.33	0.98	6.65
1973	37.0	9.35	0.98	7.07
1974	41.0	15.0	1.11	7.06
1975	67.5	14.5	1.06	7.20
1980	113.0	17.8	1.26	12.90
1985	170.0	19.1	1.52	18.90

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a/ Tanks, liquid HCN, 98% works.

b/ Drums, briquettes or granulated, 99% minimum, 24,000-lb lots, delivered.

c/ Drums, 20,000-lb lots, delivered, 99% minimum.

d/ Bags, regular grade, ton lots, delivered.

e/ Domestic production of NaCN for merchant sales excluding exports.

Source: U.S. Department of Commerce, Bureau of the Census, Series M28A-13; MRI estimates.

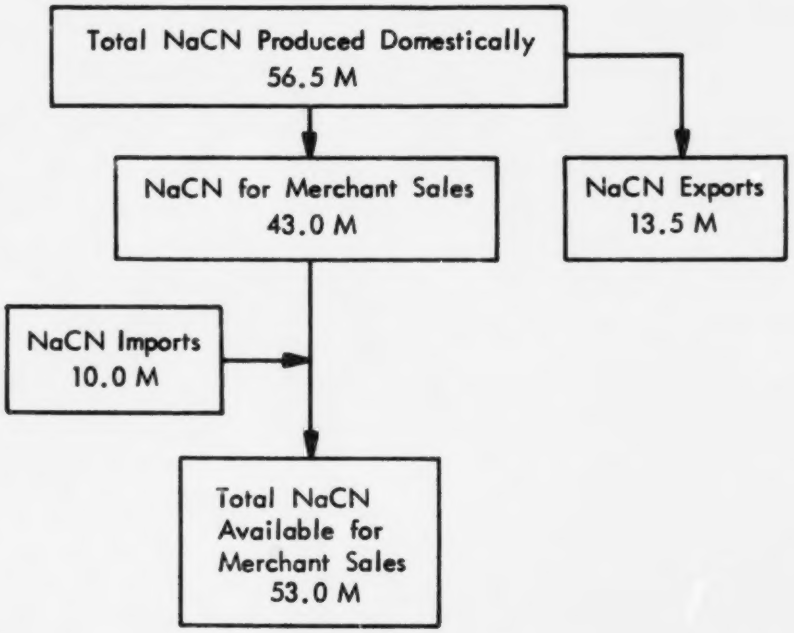
Total NaCN Produced Domestically
56.5 M
NaCN for Merchant Sales
43.0 M
NaCN Exports
13.5 M
NaCN Imports
10.0 M
Total NaCN
Available for
Merchant Sales
53.0 M

Figure 3. NaCN production, importation, and exportation in 1975 (million lb)

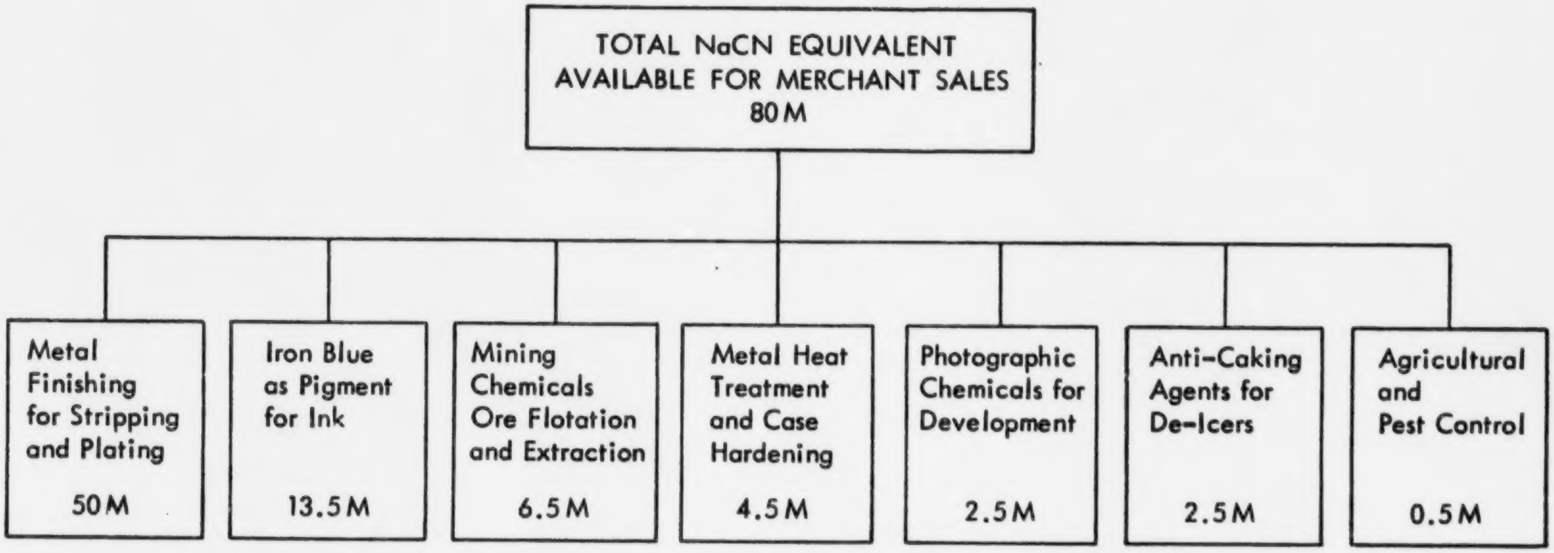
TOTAL NaCN EQUIVALENT AVAILABLE FOR MERCHANT SALES 80 M
Metal Finishing for Stripping and Plating 50 M
Iron Blue as Pigment for Ink 13.5 M
Mining Chemicals Ore Flotation and Extraction 6.5 M
Metal Heat Treatment and Case Hardening 4.5 M
Photographic Chemicals for Development 2.5 M
Anti-Caking Agents for De-Icers 2.5 M
Agricultural and Pest Control 0.5 M

Figure 4. Distribution of NaCN equivalent available for merchant sales (million lb)

The term "NaCN equivalent" refers to the fact that some NaCN is consumed as a raw material for the production of other metal cyanides, e.g., ferro- and ferricyanides and heavy metal cyanides. Consumption of NaCN equivalent in these areas is estimated at 27 million pounds in 1975 as heavy metal cyanides, iron blue pigment, photographic chemicals, anti-caking agents, mining chemicals, and for agricultural and pest control.

Large amounts of NaCN are used directly in electroplating baths, metal heat treating salt baths, and as a mining chemical. Consumption of NaCN in these areas is estimated at 53 million pounds. Thus, total consumption is 80 million pounds of NaCN equivalent in the merchant sector.

The previous information on NaCN was utilized to develop Table 6 for the years 1965 to 1985 inclusive. Exports and imports for the years 1965 to 1973 inclusive are accurately known; all other data are estimates. Merchant sales plus imports were assumed to increase 3% annually from 1965 to 1969, with no growth from 1970 to 1972. Projections to 1985 are based on a decline in sodium cyanide usage due to introduction of noncyanide processes and materials; e.g., noncyanide plating baths and gaseous carbo-nitriding for case hardening metals.

E. I. du Pont de Nemours and Company is the principal manufacturer of sodium and potassium cyanide and guard the production figures of each. However, Mr. James McNutt and Mr. Robert Pieslik of the Industrial Chemicals Department assisted this survey by providing a limited amount of information on these chemicals.[4,5]

Potassium Cyanide

Production of potassium cyanide for merchant sales is also an unknown quantity but has been estimated at 7% of domestic production of sodium cyanide for merchant sales and imports. Table 7 presents estimated domestic production of potassium cyanide for merchant sales plus importation data. The figures for domestic production are corroborated by a Du Pont source which estimated production at less than 5 million pounds annually.[5] Imports are known accurately for 1965 to 1973; potassium cyanide is not exported in significant quantities.

Calcium Cyanide

There are no sources for domestically produced calcium cyanide. American Cyanamid Company imports large amounts of this chemical from its affiliate in Canada. Degussa, Inc., also imports calcium cyanide from Europe.

Table 6. ESTIMATED DOMESTIC PRODUCTION OF NaCN FOR MERCHANT SALES
(million lb annually)

Year	Domestic production for merchant sales	Exports	Imports	Domestic production for merchant sales plus imports	Domestic production for merchant sales plus exports
1965	32.0	8.5	21.5	53.5	40.5
1966	34.0	8.1	20.9	54.9	42.1
1967	35.0	10.2	21.4	56.4	45.2
1968	38.3	11.4	19.7	58.0	49.7
1969	45.0	12.3	14.7	59.7	57.3
1970	42.8	23.0	18.7	61.5	65.8
1971	46.1	18.3	13.9	60.0	64.4
1972	41.1	8.7	17.2	58.3	49.8
1973	45.1	12.0	11.6	56.7	57.1
1974	45.1	12.5	10.0	55.1	57.6
1975	43.0	13.5	10.0	53.0	56.5
1980	38.0	16.0	10.0	48.0	54.0
1985	32.0	19.0	10.0	42.0	51.0

Note: Data on exports and imports from Bureau of the Census for 1965 to 1973. Exports to grow by 5%/year 1975 to 1985. Imports to remain unchanged.

Table 7. ESTIMATED DOMESTIC PRODUCTION OF KCN FOR MERCHANT SALES
(million lb annually)

Year	Domestic production for merchant sales	Imports	Exports	Domestic production plus imports
1965	1.7	2.2	0	3.9
1966	1.7	2.3	0	4.0
1967	2.0	1.9	0	3.9
1968	2.2	1.8	0	4.0
1969	2.1	2.1	0	4.2
1970	2.3	1.9	0	4.2
1971	2.5	1.4	0	3.9
1972	2.3	1.6	0	3.9
1973	2.3	1.5	0	3.8
1974	2.1	1.7	0	3.8
1975	2.0	1.6	0	3.6
1980	1.7	1.6	0	3.3
1985	1.6	1.6	0	3.2

Note: KCN domestic production and imports set at 7% of the corresponding NaCN domestic production for merchant sales and imports. MRI estimates.

Iron Blue

The production history of iron blue is readily obtainable, and manufacturers are relatively open on this subject. Table 3 presents production data and Figure 5 presents total consumption data for iron blue with projection estimates to 1985. This information was gathered with the assistance of representatives from American Cyanamid Company, Reichhold Chemicals, Inc., and the Bureau of Mines.[6-8]

Table 8 presents current and former manufacturers of iron blue and the estimated market share of the two principal manufacturers.

Heavy Metal Cyanides, Including Ferro- and Ferricyanides

Table 9 presents a listing of various cyanide salts including heavy metal cyanide manufacturers and distributors. Those companies with an enclosed symbol (D) are former distributors.

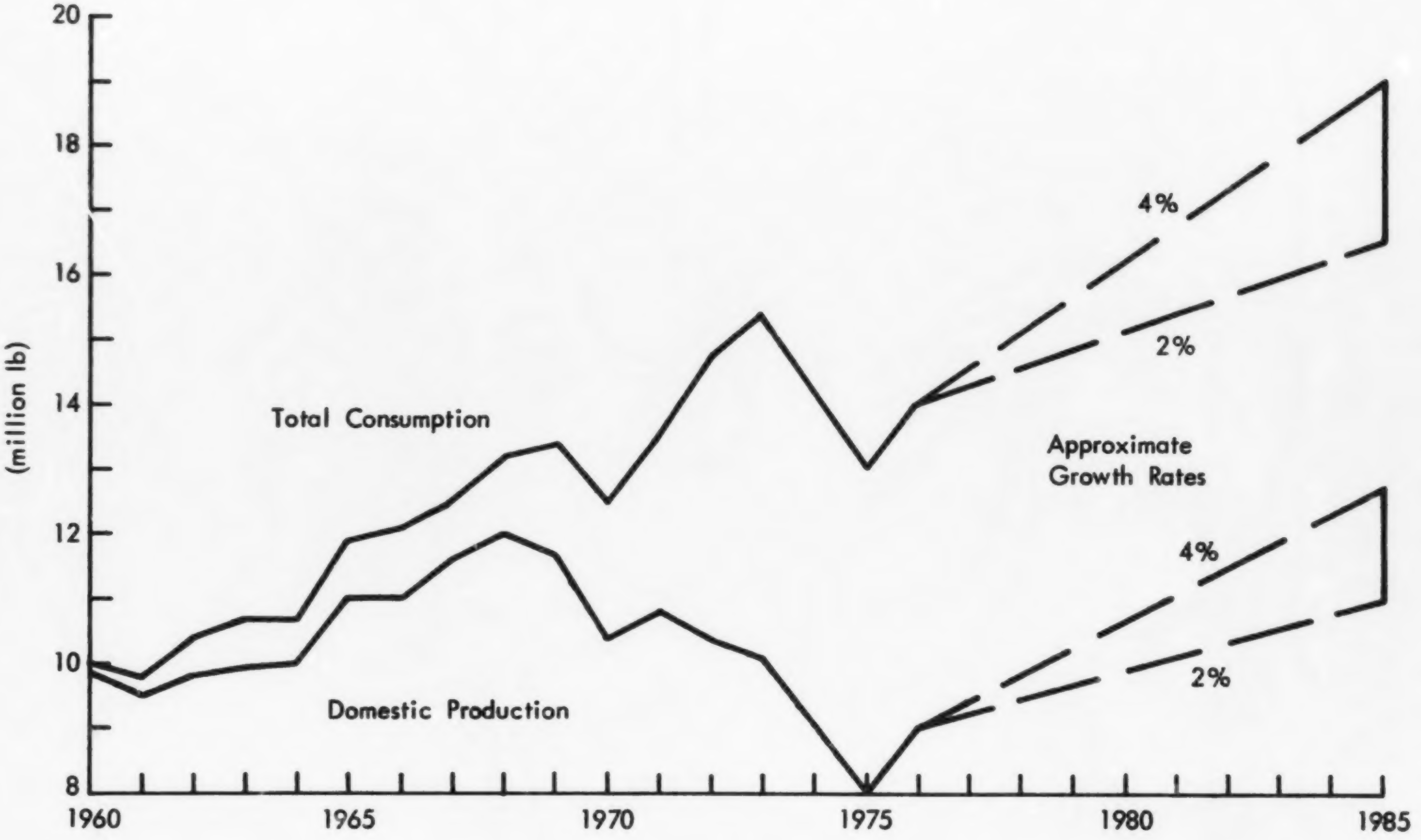

Figure 5. Iron blue consumption

Table 8. CURRENT AND FORMER MANUFACTURERS OF IRON BLUE

Company	Location	Comment	Estimated market (%)
American Cyanamid Company Pigments Division	Willow Island, West Virginia	Principal manufacturer	≃ 70
Hercules, Inc. Imperial Division	Glens Falls, New York	Principal manufacturer	≃ 25
The Harshaw Chemical Company Pigments and Dye Department	Louisville, Kentucky	Alkali-resistant grade manufacturer	≤ 5
Chemetron Corporation	Holland, Michigan	Discontinued 1973	
E. I. du Pont de Nemours and Company, Inc. Pigments Department	Wilmington, Delaware	Discontinued 1965	
Hilton-Davis Chemical Company	Cincinnati, Ohio	Discontinued 1972	
H. Kohnstamm and Company, Inc.	New York, New York	Discontinued 1970	
Reichhold Chemicals, Inc.	White Plains, New York	Discontinued 1972	

Table 9. MAJOR COMPANIES MANUFACTURING AND/OR DISTRIBUTING CYANIDE SALTS FOR INDUSTRIAL USE

Metal cyanide	Company	Location	Manufacturer, distributor
NaCN	Ashland Chemical Company	Columbus, Ohio	D
	C. P. Chemicals, Inc.	Sewaren, New Jersey	D
	Degussa, Inc. (import)	New York, New York	D
	E. I. du Pont de Nemours and Company, Inc.	Memphis, Tennessee	M,D
	Fisher Scientific Company	Fair Lawn, New Jersey	M,D
	Harshaw Chemical Company	Cleveland, Ohio	D
	Imperial Chemical Industries, Ltd. (import)	Wilmington, Delaware	D
	J. T. Baker Chemical Company	Phillipsburg, New Jersey	D
	M&T Chemicals, Inc.	Rahway, New Jersey	D
	Phillips Brothers Chemical Company	New York, New York	D
	Sobin Chemicals, Inc.	Boston, Massachusetts	D
	United Mineral and Chemical Corporation	New York, New York	(D)[a]
KCN	Ashland Chemical Company	Columbus, Ohio	D
	C. P. Chemicals, Inc.	Sewaren, New Jersey	D
	Degussa, Inc. (import)	New York, New York	D
	E. I. du Pont de Nemours and Company, Inc.	Memphis, Tennessee	M,D
	Fisher Scientific Company	Fair Lawn, New Jersey	M,D
	Harshaw Chemical Company	Cleveland, Ohio	D
	Harstan Chemical Company	Brooklyn, New York	D
	Imperial Chemical Industries, Ltd. (import)	Wilmington, Delaware	D
	J. T. Baker Chemical Company	Phillipsburg, New Jersey	D
	Mallinckrodt Chemical Company	St. Louis, Missouri	M,D
	M&T Chemicals, Inc.	Rahway, New Jersey	D
	Phillips Brothers Chemical Company	New York, New York	D
	United Mineral and Chemical Corporation	New York, New York	(D)

Table 9. (continued)

Metal cyanide	Company	Location	Manufacturer, distributor
$Ca(CN)_2$	American Cyanamid Company (import)	Wayne, New Jersey	M,D
	Degussa, Inc. (import)	New York, New York	D
$Cd(CN)_2$	City Chemical Corporation	New York, New York	M,D
Ferrocyanide	American Cyanamid Company	Wayne, New Jersey	M,D
	Ashland Chemical Company	Columbus, Ohio	D
	Hercules, Inc.	Glens Falls, New York	M
	Mallinckrodt Chemical Company	St. Louis, Missouri	M,D
	Philip A. Hunt Chemical Company	Palisades Park, New Jersey	(D)
	United Mineral and Chemical Corporation	New York, New York	(D)
Ferricyanide	American Cyanamid Company	Wayne, New Jersey	M,D
	Degussa, Inc. (import)	New York, New York	D
	Eastman Kodak Copmany	Rochester, New York	M,D
	Mallinckrodt Chemical Company	St. Louis, Missouri	M,D
	Philip A. Hunt Chemical Company	Palisades Park, New Jersey	D
	United Mineral and Chemical Corporation	New York, New York	D
CuCN	Ashland Chemical Company	Columbus, Ohio	D
	E. I. du Pont de Nemours and Company, Inc.	Niagara Falls, New York	M,D
	Fisher Scientific Company Ltd.	Fair Lawn, New Jersey	M,D
	Harshaw Chemical Company	Cleveland, Ohio	D
	Harstan Chemical Company	Brooklyn, New York	D
	Imperial Chemical Industries, Ltd. (import)	Wilmington, Delaware	D
	Phillips Brothers Chemical Company	New York, New York	M,D

Table 9. (concluded)

Metal cyanide	Company	Location	Manufacturer, distributor
$Zn(CN)_2$	Ashland Chemical Company	Columbus, Ohio	D
	C. P. Chemicals, Inc.	Sewaren, New Jersey	M,D
	E. I. du Pont de Nemours and Company, Inc.	Niagara Falls, New York	M,D
	Harstan Chemical Company	Brooklyn, New York	D
	Imperial Chemical Industries, Ltd. (import)	Wilmington, Delaware	D
	Phillips Brothers Chemical Company	New York, New York	M,D
$Na(K)Cu(CN)_2$	Ashland Chemical Company	Columbus, Ohio	D
	C. P. Chemicals, Inc.	Sewaren, New Jersey	M,D
	E. I. du Pont de Nemours and Company, Inc.	Niagara Falls, New York	M,D
	Harstan Chemical Company	Brooklyn, New York	M,D
AgCN	Ashland Chemical Company	Columbus, Ohio	D
	Engelhard Industries, Inc.	Newark, New Jersey	M,D
	Fisher Scientific Company, Ltd.	Fair Lawn, New Jersey	M,D
	Mallinckrodt Chemicals Company	St. Louis, Missouri	M,D
$KAu(CN)_2$	Ashland Chemical Company	Columbus, Ohio	D
	Engelhard Industries, Inc.	Newark, New Jersey	M,D
	Fisher Scientific Company	Fair Lawn, New Jersey	M,D

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a/ ( ) Denotes former distributor.

The production history of ferro- and ferricyanides and of heavy metal cyanides, principally zinc, cadmium, copper, gold, and silver cyanides, is largely unknown at present. Companies such as CP Chemicals, Inc., and E. I. Du Pont are producers of metal cyanides such as copper, zinc, and the double salts of these metals, i.e., sodium copper cyanide, sodium zinc cyanide, etc., but consider their production statistics confidential information.

Trade and professional associations such as the American Electroplaters' Society, The Silver Institute, Metal Finishing Magazine, Manufacturing Chemists Association, Metal Finishing Suppliers Association, etc., simply do not possess consumption data on cyanides. Representatives from these organizations were sympathetic to the needs of the survey, but could offer no data on industry usage rates and/or considered this proprietary information. Typical of comments from Metal Finishing Magazine editor Nathaniel Hall, was the following:

> "I can sympathize with your obvious frustration at the lack of any figures . . . of chemical usage in the finishing industry. You are not the first since, unfortunately, no one has even been able to compile any figures in our industry, aside from a handful of chemicals and metals."[9]

Thus, due to lack of hard data, it is not possible at present to develop complete tables of production statistics for ferro- and ferricyanides and other heavy metal cyanides and arrive at an estimate of capital value for these chemicals.

In order to calculate a total cyanide material balance in Chapter V it will be necessary to estimate the 1975 heavy metal cyanide consumption in the electroplating sector using data from various sources. Table 10 presents annual consumption of NaCN, KCN, and heavy metal cyanides in the electroplating sector. The consumption estimates of the various cyanides are reduced to a common basis, NaCN equivalent weight. This is reasonable since NaCN is the principal constituent of all plating baths except gold and high-speed copper.

Bath makeup occurs at initial start-up and is repeated on rare occasions due to accidental dumping, leakage, and contamination. Soluble anodes are generally used in conjunction with direct NaCN additions. Estimated heavy metal cyanide consumption is about 10 million pounds or 7.3 million pounds of NaCN equivalent.

Table 10. SODIUM CYANIDE EQUIVALENT CONSUMPTION IN METAL FINISHING IN 1975[a]

Category I - Bath makeup

	Metal cyanide (million lb)		Consumption as NaCN equivalent (million lb)
	7.0 $Zn(CN)_2$		5.8
	1.5 CuCN		0.8
	0.6 $Cd(CN)_2$		0.4
	0.5 AgCN		0.2
	0.2 $KAu(CN)_2$[11]		0.07
Subtotal	9.8	Subtotal	7.3

Category II - Plating bath maintenance

Metal cyanide plating process	Metal consumed in plating (million lb)	Maintenance requirements by NaCN		
Zinc	~ 100 Zn	~ 30%		30
Copper and brass[10]	10 Cu	~ 25-30%		3.0[b]
Cadmium[10]	4.4 Cd	~ 25-30%		1.2
Silver[11]	2.4 Ag	~ 30-50%		1.0
Gold (jewelry)	0.01 Au	~ 10X		0.1
			Subtotal	35.3

Category III - Stripping, cleaning, deburring, tumbling, etc.

	8
Total	50.6

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[a] Source: MRI estimate.

[b] Includes 0.3 M KCN.

IMPORTATION AND CAPITAL VALUE

Importation is generally confined to the following cyanides: sodium cyanide, potassium cyanide, sodium ferrocyanide, potassium ferrocyanide, potassium ferricyanide, calcium cyanide and iron blue (ferric-ammonium ferrocyanide).

Various heavy metal cyanides, e.g., cuprous cyanide, zinc cyanide, mercury cyanide, etc., are imported in relatively small quantities; less than 1 million pounds each and having capital values of less than $1 million each. Other cyanides are classed merely as Mixtures of Inorganic Compounds, Chief Value Cyanide, TSUSA No. 423820 and are of negligible amounts.

Tables 11 through 14 present importation data and capital value for various cyanides over the years 1965 to 1973 inclusive with extrapolations for the years 1974, 1975, 1980, and 1985. From 1975 to 1985, a linear price rise of 8% annually was assumed. It may be seen that large amounts of various cyanides have been imported in the past.

As developed earlier in Chapter V, the quantity of NaCN equivalent used industrially is very large, of the order of 80 ± 6.6 million pounds annually. Present imports account for nearly 29 million pounds of NaCN equivalent annually. The estimated amount of cyanides imported in 1975 is given in Table 15 for purposes of summary.

Figure 6 presents the cyanide importation historical record for the years 1960 to 1973 inclusive with projections to 1985. In the past, much calcium cyanide has been imported, principally by American Cyanamid Company from its Canadian operation at Niagara Falls. Over the years 1960 to 1970 inclusive some 200 million pounds of calcium cyanide were imported for an average of 33 million pounds annually. However, in 1971 and the following years importation dropped to less than 10 million pounds annually. American Cyanamid Company told us that the plant was voluntarily shut down when the Canadian government imposed effluent restructions on the operation. This decision was also influenced by rapidly rising power costs required to operate the electric furnaces which convert calcium cyanamid to calcium cyanide.

After some period of negotiations, American Cyanamid Company and the Canadian government agreed to jointly fund the necessary modifications to allow the plant to come back on stream. Beginning in 1975 the flow of calcium cyanide from Canada should rise somewhat, but probably will not match the previous historical record because of a projected decrease in overall industrial cyanide demand. This opinion differs from one source at American Cyanamid who suggested that the importation rate would return to the level of 20 to 30 million pounds annually by 1980-1985.[12]

Table 11. CYANIDE IMPORTS AND CAPITAL VALUE - SODIUM SALTS

	Sodium cyanide		Sodium ferrocyanide		Total	
Year	Million pounds	Million dollars	Million pounds	Million dollars	Million pounds	Million dollars
1965	21.5	2.62	3.4	0.45	24.9	3.07
1966	20.9	2.46	5.7	0.60	26.6	3.06
1967	21.4	2.64	6.4	0.66	27.8	3.30
1968	19.7	2.48	6.5	0.67	26.2	3.15
1969	14.7	1.89	5.0	0.54	19.7	2.43
1970	18.7	2.42	4.0	0.41	22.7	2.83
1971	13.9	1.94	3.0	0.32	16.9	2.26
1972	17.2	2.47	1.8	0.22	19.0	2.69
1973	11.6	1.73	0.4	0.06	12.0	1.79
1974	14.4	2.70	0.5	0.08	14.9	2.78
1975	10.0	2.02	0.5	0.08	10.5	2.10
1980	10.0	2.84	1.0	0.23	11.0	3.07
1985	10.0	3.64	1.0	0.29	11.0	3.93

Source: U.S. Department of Commerce, Bureau of the Census, FT 246, MRI estimates.

Table 12. CYANIDE IMPORTS AND CAPITAL VALUE - POTASSIUM SALTS

	Potassium cyanide		Potassium ferrocyanide		Potassium ferricyanide		Total	
Year	Million pounds	Million dollars	Million pounds	Million dollars	Million pounds	Million dollars	Million pounds	Million dollars
1965	2.2	0.51	2.3	0.47	1.3	0.41	5.8	1.39
1966	2.3	0.54	4.3	0.80	1.3	0.41	7.9	1.75
1967	1.9	0.40	3.8	0.71	1.3	0.41	7.0	1.52
1968	1.8	0.41	4.4	0.94	1.6	0.52	7.8	1.87
1969	2.1	0.44	1.5	0.27	2.1	0.67	5.7	1.38
1970	1.9	0.41	2.4	0.46	1.5	0.46	5.8	1.33
1971	1.4	0.30	2.1	0.39	1.7	0.59	5.2	1.28
1972	1.6	0.36	2.0	0.42	2.1	0.73	5.7	1.51
1973	1.5	0.36	1.8	0.44	1.4	0.58	4.7	1.38
1974	1.7	0.44	1.7	0.45	1.7	0.76	5.1	1.67
1975	1.6	0.45	1.7	0.48	1.7	0.82	5.0	1.75
1980	1.6	0.63	1.7	0.68	1.7	0.87	5.0	2.18
1985	1.6	0.81	1.7	0.87	1.7	0.93	5.0	2.61

Source: U.S. Department of Commerce, Bureau of the Census, FT 246, MRI estimates.

Table 13. CALCIUM CYANIDE IMPORTS AND CAPITAL VALUE

	Calcium cyanide	
Year	Million pounds	Million dollars
1965	35.8	1.46
1966	35.3	1.44
1967	33.0	1.35
1968	32.3	1.32
1969	32.4	1.29
1970	31.6	1.31
1971	10.9	0.46
1972	4.9	0.28
1973	7.8	0.58
1974	7.5	0.61
1975	8.0	0.71
1980	9.0	1.13
1985	10.0	1.62

Source: U.S. Department of Commerce, Bureau of the Census,
MRI estimates.

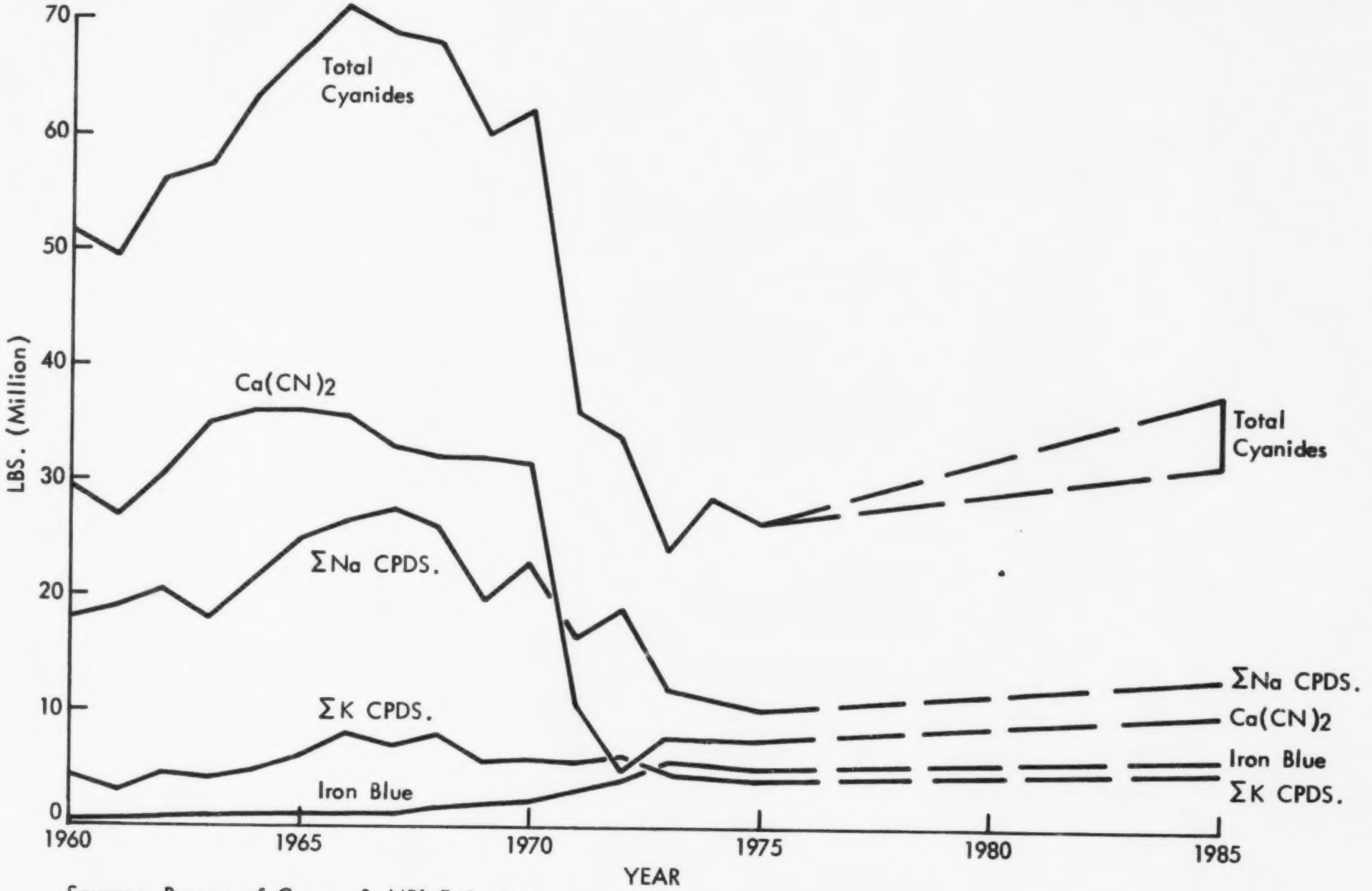
Table 14. IRON BLUE CONSUMPTION, IMPORTATION, AND CAPITAL VALUE

	Domestic		Imports		Totals	
Year	Million pounds	Capital value ($)	Million pounds	Capital value ($)	Million pounds	Capital value ($)
1965	11.0	6.16	0.9	0.40	11.9	6.56
1966	11.1	6.32	1.1	0.48	12.2	6.80
1967	11.6	6.73	0.9	0.40	12.5	7.13
1968	12.1	7.26	1.2	0.50	13.3	7.76
1969	11.7	7.26	1.7	0.63	13.4	7.89
1970	10.4	7.06	2.1	0.87	12.5	7.93
1971	10.8	6.80	2.7	1.04	13.5	7.84
1972	10.4	6.65	4.3	1.65	14.7	8.30
1973	10.1	7.07	5.3	2.21	15.4	9.28
1974	9.0	7.06	5.1	2.50	14.1	9.56
1975	8.0	7.20	5.0	2.50	13.0	9.70
1980	10.3	12.90	5.3	3.70	15.6	16.60
1985	11.8	18.90	6.0	5.40	17.8	24.30

Source: U.S. Department of Commerce, Bureau of Census, FT 246, M28A-13, MRI Estimates.

Table 15. ESTIMATED CYANIDE IMPORTATION IN 1975

	(million lb)		
Cyanide	Quantity	NaCN Equivalent	Principal exporting countries
NaCN	10.0	10.0	U.K., West Germany, Japan
KCN	1.6	1.2	Canada, Japan
$Ca(CN)_2$	8.0	8.5	U.K., Japan
Iron blue	5.0	5.2	Europe, U.K., Japan
Heavy metal and ferro- and ferricyanides	≃ 5.0	≃ 3.7	U.K., West Germany, Japan
Total	29.6	28.6	



Source: Bureau of Census & MRI Estimates

Figure 6. Cyanide importation

EXPORTATION AND CAPITAL VALUE

Exportation of cyanides is essentially confined to sodium cyanide. No other separate cyanide listing was given by the Bureau of the Census. Principal areas or countries receiving sodium cyanide are South America, United Kingdom, Canada, and Mexico. The historical data and capital value are given in Figures 7 and Table 16. A linear rise of 5% annually is projected for NaCN exportation.

USAGE PATTERNS

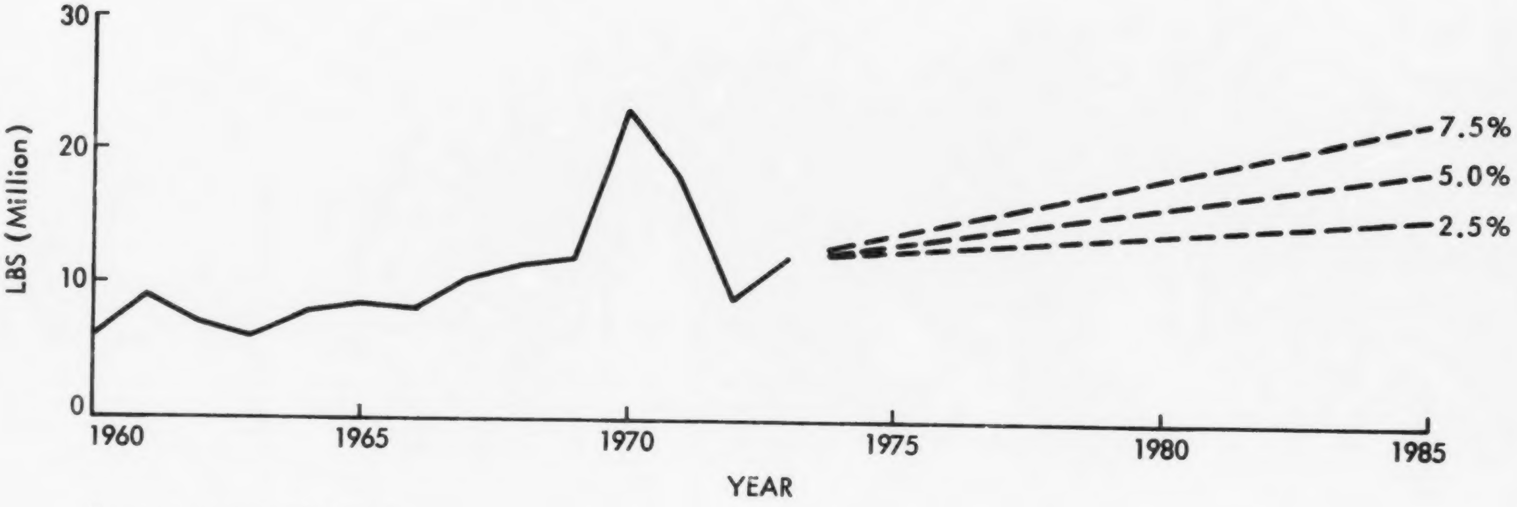
The cyanides of sodium and calcium as well as hydrogen cyanide gas have been used extensively as agricultural and pest control chemicals in the past but this is no longer true. The use of cyanides in these areas has all but disappeared and likely will not return. Data in the Encyclopedia of Chemical Technology by Kirk and Othmer are largely incorrect in this area.[13]

Sodium cyanide and to a much smaller extent calcium cyanide and sodium ferrocyanide are used directly as mining chemicals for flotation and ore extraction. Sodium cyanide is also added directly to electroplating baths for replenishment. Aside from these three examples; agricultural, mining, and for plating bath maintenance, cyanides are not used as final products but instead are the raw materials for the manufacture of other products.

Cyanides find use in the preparation of electroplating baths, metal heat treatment and case hardening baths, photographic chemicals, pigments, inks, metal strippers, paints to a limited extent, and a host of organic compounds, e.g., pharmaceuticals, plastics, agricultural chemicals, chelating agents, and other organic intermediates. Essentially all cyanides are derived from hydrogen cyanide today except for calcium cyanide which is made from calcium cyanamid.

The Chemical Marketing Reporter estimates of hydrogen cyanide usage patterns are given in Table 17.

The range for NaCN usage is between 7 to 10% of HCN production over the last 12 years. The organic sector will probably consume 90% of HCN production with NaCN being produced in the largest quantity in the inorganic sector to 1985.



Source: Bureau of Census

Figure 7. NaCN exportation

Table 16. SODIUM CYANIDE EXPORTS

Year	NaCN Million pounds	NaCN Million dollars
1965	8.5	1.29
1966	8.1	1.15
1967	10.3	1.41
1968	11.4	1.67
1969	12.3	1.58
1970	23.0	2.79
1971	18.3	2.61
1972	8.7	1.42
1973	12.0	2.16
1974	16.2	3.93
1975	13.5	2.97
1980	16.0	4.80
1985	19.0	7.60

Source: U.S. Department of Commerce, Bureau of Census, FT 410, MRI Estimates.

Table 17. USAGE PATTERNS FOR HYDROGEN CYANIDE (%)

Date[a]	Adiponitrile	Acrylonitrile	Methyl methacrylate	Acrylic acid	Chelates	NaCN	Other
May 27, 1963	14	52	18	1	-	7	8
May 22, 1967	-	34	38	5	8	10	5
October 5, 1970	-	-	61	-	21	10	8
December 10, 1973	-	-	61	-	21	10	8

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[a] Ref. 4, Chapter VI.

FINAL PRODUCTS AND DISPOSAL

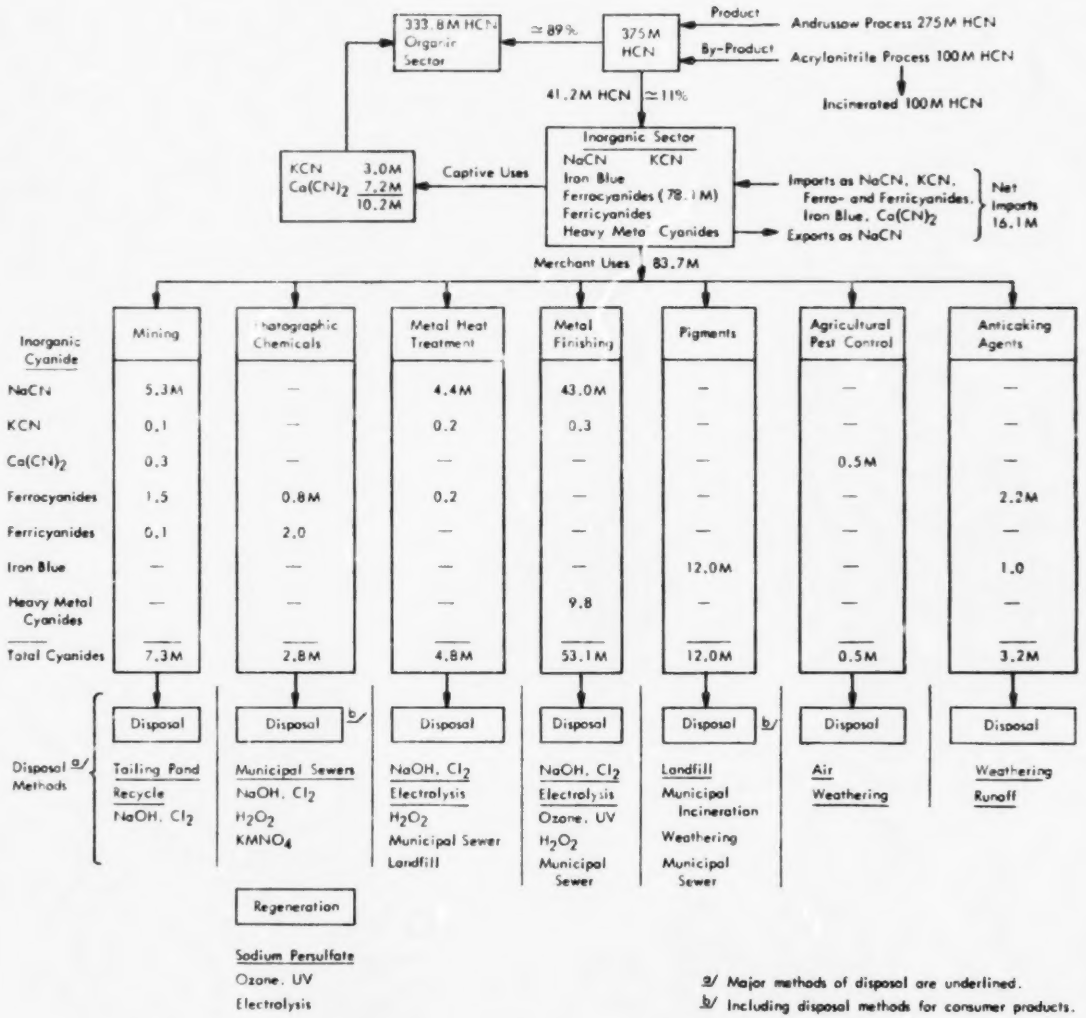
As stated earlier cyanides are not generally used as final products except for flotation and ore extraction, for electroplating bath replenishment, as anti-caking agents, and as agricultural and pest control chemicals. Cyanides are used extensively as raw materials in proprietary plating baths, case hardening metal heat treating baths, as photographic chemicals, as pigments for paints, inks, carbon papers, and as colorants in plastics.

Hydrogen cyanide principally enters the organic sector as a raw material in the manufacture of a host of organic chemicals. Sodium cyanide is derived from hydrogen cyanide and is used in large quantities in proprietary plating baths, in metal heat treating baths, and as a direct replenishment chemical as stated above. Calcium cyanide is used directly for mining applications but is more generally used for organic synthesis purposes and to make other metal cyanides, e.g., ferro- and ferricyanides. Iron blue is made from ferrocyanides. Heavy metal cyanides are made from sodium cyanide and the corresponding metal ion or by reacting metal ion with hydrocyanic acid.

Some idea of the vastness of the use of sodium cyanide and other merchant cyanides as industrial chemicals is shown in Figure 8. The industrial applications are many in the metal finishing and electroplating sector and include electronic, jewelry, automotive, aircraft, and consumer items. The figure indicates captive use of potassium cyanide and calcium cyanide for organic synthesis purposes. The route of each metal cyanide from introduction through consumption and ultimate destruction and disposal is given explicitly on a weight basis.

Iron blue appears to be a chemical that is not of great concern at present due to its innocuous nature. Thus, iron blue may enter the industrial sector as pigment for ink, carbon paper, or as trash bag colorant. Ultimately, iron blue enters the consumer sector and reaches the municipal waste collection system where it is incinerated or becomes part of landfill. A portion of iron blue enters the environment directly as an anticaking agent in highway de-icing operations.

One study indicated that the action of UV illumination of ferro- and ferricyanides in solution can generate significant amounts of cyanide ion.[14/] A similar study for iron blue has not been performed nor has an incineration study of iron blue to determine if noxious gases are liberated been carried out to our knowledge.


333.8M HCN Organic Sector
≃ 89%
375M HCN
Product
By-Product
Andrussow Process 275M HCN
Acrylonitrile Process 100M HCN
Incinerated 100M HCN
41.2M HCN
≃ 11%
Inorganic Sector
NaCN
KCN
Iron Blue
Ferrocyanides (78.1M)
Ferricyanides
Heavy Meta Cyanides
Captive Uses
KCN 3.0M
Ca(CN)2 7.2M
10.2M
Imports as NaCN, KCN, Ferro- and Ferricyanides, Iron Blue, Ca(CN)2
Exports as NaCN
Net Imports 16.1M
Merchant Uses 83.7M
Inorganic Cyanide
NaCN
KCN
Ca(CN)2
Ferrocyanides
Ferricyanides
Iron Blue
Heavy Metal Cyanides
Total Cyanides
Mining
5.3M
0.1
0.3
1.5
0.1
—
—
7.3M
Photographic Chemicals
—
—
—
0.8M
2.0
—
—
2.8M
Metal Heat Treatment
4.4M
0.2
—
0.2
—
—
—
4.8M
Metal Finishing
43.0M
0.3
—
—
—
—
9.8
53.1M
Pigments
—
—
—
—
—
12.0M
—
12.0M
Agricultural Pest Control
—
—
0.5M
—
—
—
—
0.5M
Anticaking Agents
—
—
—
2.2M
—
1.0
—
3.2M
Disposal
Disposal b/
Disposal
Disposal
Disposal b/
Disposal
Disposal
Disposal a/ Methods
Tailing Pond
Recycle
NaOH, Cl2
Municipal Sewers
NaOH, Cl2
H2O2
KMNO4
NaOH, Cl2
Electrolysis
H2O2
Municipal Sewer
Landfill
NaOH, Cl2
Electrolysis
Ozone, UV
H2O2
Municipal Sewer
Landfill
Municipal Incineration
Weathering
Municipal Sewer
Air
Weathering
Weathering
Runoff
Regeneration
Sodium Persulfate
Ozone, UV
Electrolysis

a/ Major methods of disposal are underlined.
b/ Including disposal methods for consumer products.

Figure 8. Inorganic cyanide consumption and disposal pattern (million pounds)

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CHAPTER VI

MANUFACTURING PROCESSES

This chapter presents manufacturing processes for hydrogen cyanide and other cyanides in detail. Two principal synthesis routes for hydrogen cyanide are the Andrussow direct process and the SOHIO-acrylonitrile process which produces the cyanide as a by-product. Manufacturers are identified by site location and capacity. The chapter closes with a discussion of manufacturing wastes disposal and transportation rates and regulations.

HYDROGEN CYANIDE

The general manufacturing process for hydrogen cyanide is the Andrussow method which is given schematically in Figure 9.[1] The method consists of passing ammonia, air, and natural gas over a platinum-rhodium catalyst at elevated temperature.[2] The net reaction is:

$$2\ NH_3 + 2\ CH_4 + 3O_2 \xrightarrow[\text{Cat.}]{1100^\circ C} 2\ HCN + 6\ H_2O$$

After reaction, the mixture is quenched to below 400°C to prevent dissociation of the hydrogen cyanide. The gaseous mixture is scrubbed with dilute sulfuric acid to remove ammonia for recycling. Hydrogen cyanide is absorbed in the water phase. The final product (99+% purity) is obtained by distillation and stabilized by addition of 0.1% phosphoric acid to prevent polymerization. The hydrogen cyanide yield is near 75% based on recycled ammonia and 65% based on methane.

Waste gases include hydrogen, nitrogen, carbon monoxide and dioxide, and water. The wastewater from the still residue is treated with caustic chlorine to yield carbon dioxide, nitrogen, and dissolved salt. Other waste disposal methodologies are employed and are mentioned later in this section.

Hydrogen cyanide is also produced as a by-product in the manufacture of acrylonitrile. Since 1970 all plants in the U.S. use the SOHIO process or some modification.[3] Figure 10 presents a schematic flow diagram of the SOHIO process for acrylonitrile with hydrogen cyanide as a by-product.[1]

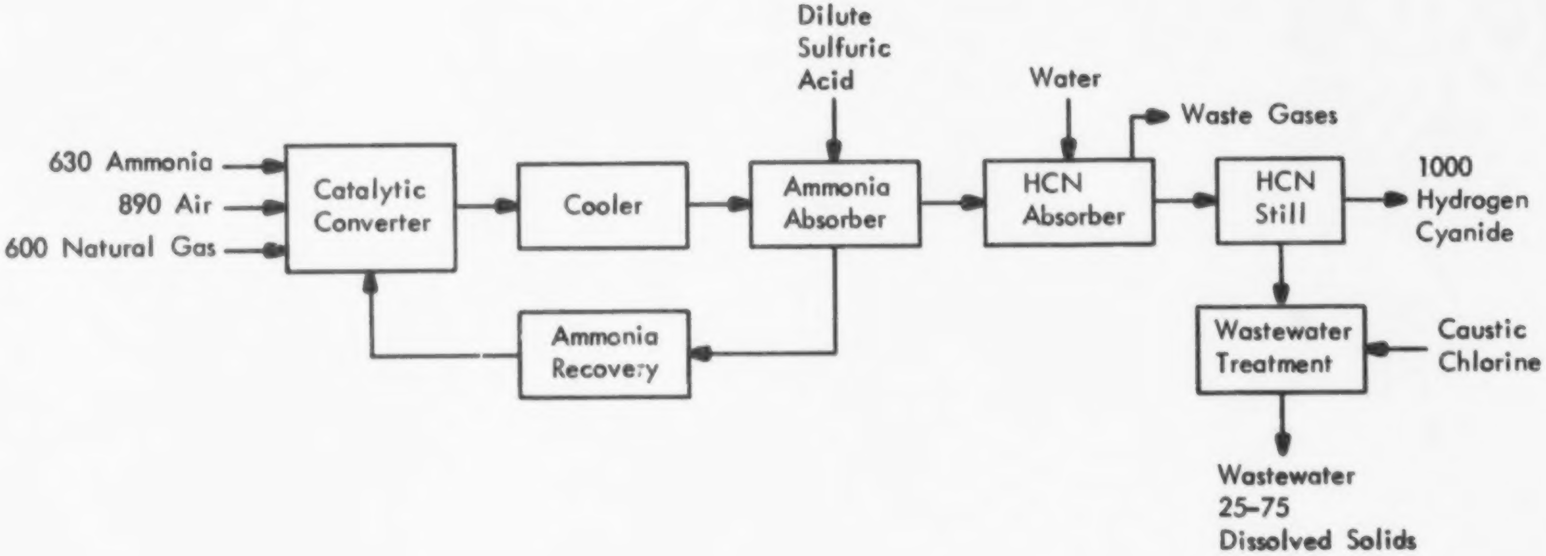
Dilute
Sulfuric
Acid
Water
Waste Gases
630 Ammonia
890 Air
600 Natural Gas
Catalytic Converter
Cooler
Ammonia Absorber
HCN Absorber
HCN Still
1000
Hydrogen
Cyanide
Ammonia Recovery
Wastewater Treatment
Caustic
Chlorine
Wastewater
25-75
Dissolved Solids

Figure 9. Manufacture of hydrogen cyanide (Andrussow process)

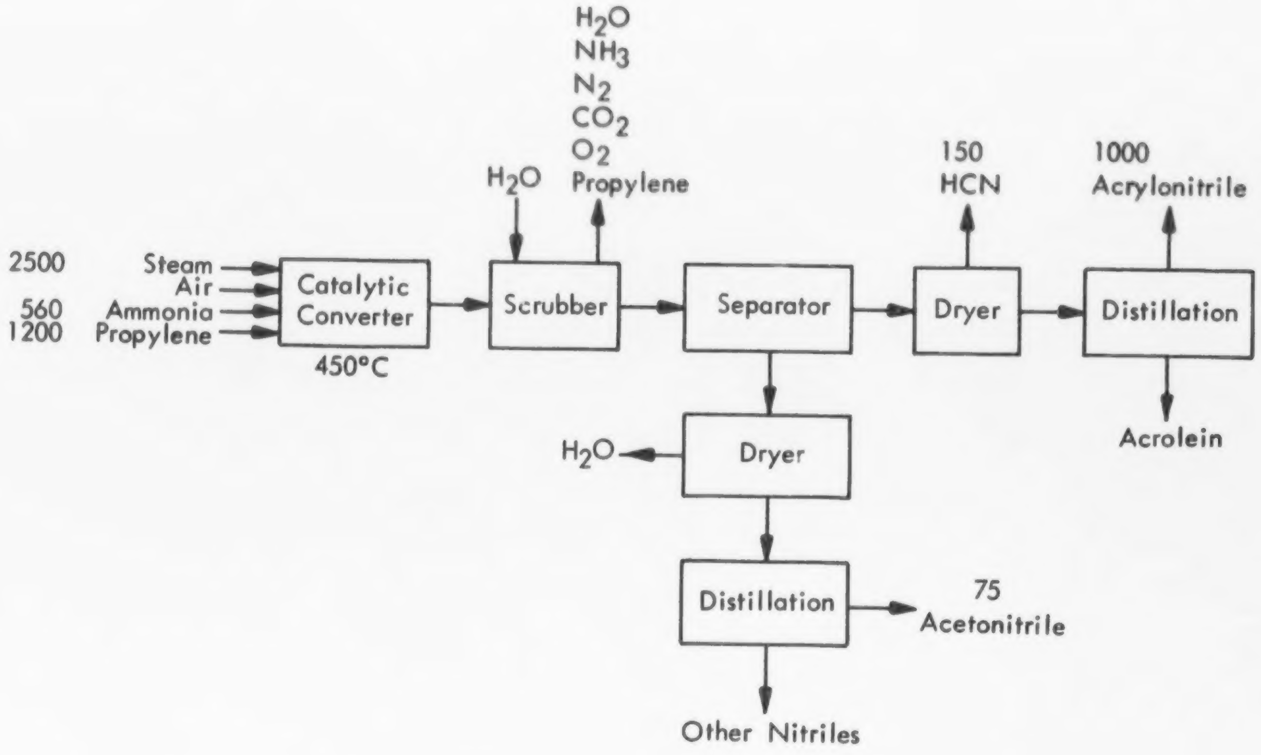
2500
560
1200
Steam
Air
Ammonia
Propylene
Catalytic Converter
450°C
H_2O
Scrubber
H_2O
NH_3
N_2
CO_2
O_2
Propylene
Separator
Dryer
H_2O
Distillation
75
Acetonitrile
Other Nitriles
Dryer
150
HCN
Distillation
1000
Acrylonitrile
Acrolein

Figure 10. Acrylonitrile (SOHIO) process for hydrogen cyanide

It is estimated that in 1975 approximately 25 to 30% of all hydrogen cyanide produced was by the SOHIO process.

In the SOHIO process propylene, ammonia, air, and steam are mixed and passed over "catalyst 41" (probably consisting of cerium and molybdenum oxides supported on a silica carrier) at 450°C. The propylene is converted to acrylonitrile in approximately 75% yield. The net reaction is:

$$2\ C_3H_6 + 2\ NH_3 + 3O_2 \xrightarrow[\text{Steam}]{450^\circ C} 2\ CH_2 = CH\text{-}CN + 6\ H_2O$$

Scrubbers remove various inert gases and unreacted propylene from the reaction effluent. The crude acrylonitrile is separated from acetonitrile, hydrogen cyanide, and water and is then distilled. Approximately 150 lb of HCN (99+% purity) are recovered for each 1,000 lb of acrylonitrile produced. If the HCN is not wanted, it is incinerated.

Some hydrogen cyanide has a transitory existence only and is immediately converted to sodium or potassium cyanide or ferrocyanides or is used for synthesis purposes internally by the producer. Hydrogen cyanide manufactured and handled in this manner is generally not counted by the Bureau of Census. The same is true for hydrogen cyanide which is incinerated. These facts account for doubt over the yearly amount of hydrogen manufactured.

The manufacturers of hydrogen cyanide are given in Table 18 and are classified as to primary (Andrussow process) or by-product (SOHIO acrylonitrile process) producers. Some companies have both kinds of operations and use hydrogen cyanide as a captive product and/or market it for merchant trade. The history is complicated since membership in this select group has radically changed over the years 1948 to 1975. Individual company capacity and production data are guarded closely. Sources for the data presented in Table 18 include the Chemical Marketing Reporter, a questionnaire circulated by Midwest Research Institute, various trade journals and publications, and contact with industry representatives.

Table 19 presents a listing of various hydrogen cyanide process waste disposal techniques. Some degree of variability exists in disposal methodology as more efficient, economic, and environmentally desirable means are sought. Alkaline chlorination is the most prevalent treatment methodology among the manufacturers, with landfill and incineration prominent.

Transportation details for all cyanides, including handling and shipping regulations, rates, and safeguards are described later in this chapter. Detailed rate data for cyanides by class and transportation mode are given in tabular form.

Table 18. MANUFACTURERS OF HYDROGEN CYANIDE BY THE ANDRUSSOW AND THE SOHIO ACRYLONITRILE PROCESSES[4]

Company	Location	Remarks	Estimated capacity (million pounds annually) 1963	1967	1970	1973	1975
American Cyanamid	South Kenner, Louisiana	B, C	-	13	27	27	27
		P, C, M 1954-1966	32	(32) Standby	(32)	(32)	(32)
Dow	Freeport, Texas	P, C, 1958-	5	5	5	5	5
Du Pont	La Place, Louisiana	P, C		20	20	20	20
	Memphis, Tennessee	P, C, M	100	115	130	130	130
	Memphis, Tennessee	B, C, M	-	-	27	27	27
	Beaumont, Texas	B, C, 1970-	-	-	30	30	30
	Victoria, Texas	P, C	40	40	40	40	40
B. F. Goodrich	Calvert City, Kentucky	B, M	5	5	7	Dis. 1972	-
Hercules	Glens Falls, New York	P, C	5	5	5	5	5
Monsanto	Texas City, Texas	P, C, 1952-	70	70	75	75	75
	Alvin, Texas	B, C	-	32	55	55	55
Rohm and Haas	Deer Park, Texas	P, C, 1948-	40	80	180	180	180
Union Carbide	Institute, West Virginia	P, C	35	35	35	Dis. 1971	-
Vistron (SOHIO)	Lima, Ohio	B, M	8	30	30	30	30
Total capacity			340	450	666	624	624

P = Primary, Andrussow Process.
B = By-product, SOHIO-acrylonitrile process.
C = Captive consumption.
M = Merchant sales.

Table 19. HYDROGEN CYANIDE PROCESS WASTE DISPOSAL TECHNIQUES

Company	Technique
American Cyanamid	Deep well injection and alkaline chlorination
Dow Chemical	-
E. I. du Pont	Calcium hypochlorite, incineration and landfill
Hercules	-
Monsanto	Alkaline chlorination and sodium hypochlorite
Rohm and Haas	Activated sludge and landfill
Vistron (SOHIO)	Deep well injection, incineration and aerobic bio-oxidation

Note: MRI source.

The capital value of a 220 million pounds per year acrylonitrile production facility has been estimated at $23 million.[5] Assuming that this estimate applies to 1970, the capital value of the same plant in 1975 may be close to $34 million.

The portion of the acrylonitrile plant capital value attributable to hydrogen cyanide is difficult to assign. In some cases the HCN may be a valuable captive or salable intermediate chemical. In other cases, the problem of its disposal may be a liability.

The capital value for a plant producing hydrogen cyanide by the Andrussow process is estimated to be $3.5 million for 50 million pounds per year capacity. This relatively low capital value results from the simple and straightforward process.

SODIUM AND POTASSIUM CYANIDE

Production of sodium and potassium cyanide is principally carried out by E. I. du Pont and Company, in Memphis, Tennessee. The neutralization process involving NaOH (or KOH) and hydrocyanic acid is schematically given in Figure 11.[1] Essentially no wastes are generated by this process as the balance between caustic and hydrocyamic acid is critical to avoid loss of cyanide values through hydrolysis. Purity of these cyanides is 99+%.

Production estimates are given in Tables 6 and 7 for NaCN and KCN, respectively. Capacity of the facilities is unknown. These data are closely guarded by E. I. du Pont de Nemours and Company and other manufacturers.

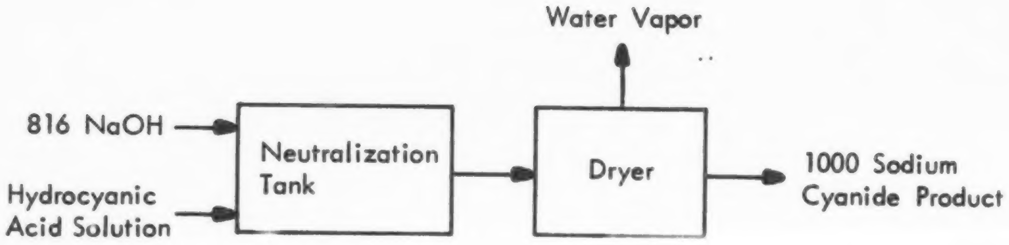
Water Vapor
816 NaOH
Neutralization Tank
Hydrocyanic Acid Solution
Dryer
1000 Sodium Cyanide Product

Figure 11. Manufacture of NaCN

Environmental management at Du Pont has been described previously in Table 19. These techniques presumably apply to sodium and potassium cyanides as well.

The capital value of a plant producing 50 million pounds of sodium cyanide and 5 million pounds of potassium cyanide per year would be $750,000 if operated in conjunction with the Andrussow hydrogen cyanide plant mentioned previously.

CALCIUM CYANIDE

American Cyanamid Company imports large amounts of calcium cyanide from Niagara Falls, Canada. The manufacturing process involves heating calcium cyanamid with coke or charcoal in a salt bath as the heat conducting medium at or near 1000°C in an electric furnace.[6] Thus,

$$CaNCN + C \xrightarrow[\text{Salt}]{1000^\circ C} Ca(CN)_2$$

Other details of this process such as capacity, materials, and energy requirements are lacking.

Presumably waste disposal methodologies for this facility are the same as those included in Table 19 for American Cyanamid Company. It is known the Canadian government and American Cyanamid are jointly involved in funding major changes in the facility to reduce pollution and emissions.

FERROCYANIDES AND FERRICYANIDES

The principal manufacturers of sodium and potassium ferro- and ferricyanides are American Cyanamid Company, Fisher Scientific Company, and the Mallinckrodt Chemical Company. The manufacture of ferrocyanides and ferricyanides is accomplished by replacement and oxidation-reduction reactions in general.[6] Thus sodium ferrocyanide is formed by combining calcium cyanide, ferrous sulfate, and sodium carbonate with water and heating with live steam:

$$3\ Ca(CN)_2 + FeSO_4 \xrightarrow[\Delta]{Na_2\ CO_3} Ca_2\ Fe(CN)_6 + CaSO_4$$

$$Ca_2\ Fe(CN)_6 + 2Na_2\ CO_3 \xrightarrow[\Delta]{} Na_4\ Fe(CN)_6 + 2CaCO_3$$

The final product as sodium ferrocyanide is obtained by evaporation, cooling, and crystallization.

Potassium ferricyanide is obtained by oxidizing potassium ferrocyanide with chlorine. Thus,

$$2\ K_4\ Fe(CN)_6 + Cl_2 \longrightarrow 2\ K_3\ Fe(CN)_6 + 2\ KCl$$

The final product is obtained by evaporation and crystallization. Alternatively, ferrocyanide may be electrolytically oxidized in a diaphragm cell with nickel electrodes.

Capacity and production data on ferro- and ferricyanides are lacking. Again, these data are held as confidential and proprietary information by manufacturers.

Environmental management and waste disposal techniques are the same as those for other cyanides except that ferro- and ferricyanides are much less toxic than the simple cyanides and landfill disposal of wastes is the most prevalent method used.

IRON BLUE

Principal manufacturers of iron blue are American Cyanamid Company at Willow Island, West Virginia, and Hercules, Inc., at Glens Falls, New York. One additional manufacturer, Harshaw Chemical Company at Lexington, Kentucky, offers a special alkali-resistant grade of iron blue but in rather small amounts, probably 500,000 lb annually.

Figure 12 illustrates the manufacture of iron blue. Sodium ferrocyanide, ferrous sulfate, and ammonium sulfate are combined in aqueous solution which is heated with live steam.[1/] A white precipitate of ferrous ammonium ferrocyanide, Berlin white, is obtained. The slurry is transferred to a heated digestion tank which contains dilute sulfuric acid to leach out soluble salts. The reaction tank may then be recharged.

After digestion, the slurry is transferred to an oxidation tank wherein sodium chlorate is added to oxidize the ferrous ion to the ferric condition. Thus, the overall reactions are:

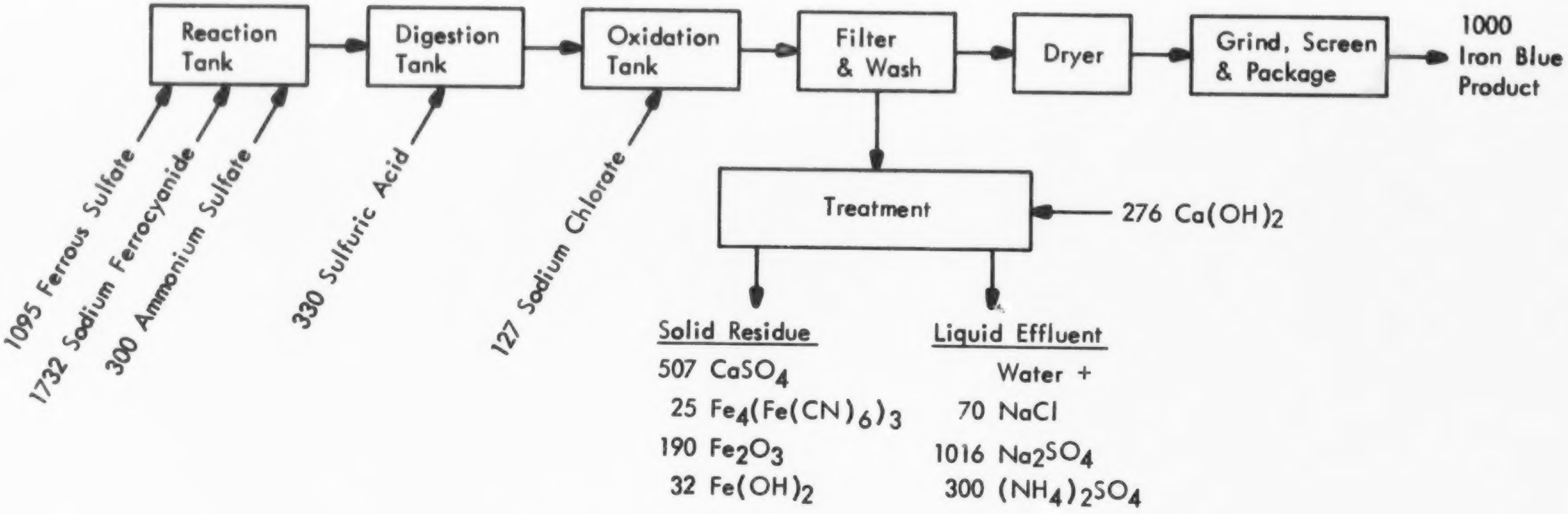
Reaction Tank
Digestion Tank
Oxidation Tank
Filter & Wash
Dryer
Grind, Screen & Package
1000 Iron Blue Product
1095 Ferrous Sulfate
1732 Sodium Ferrocyanide
300 Ammonium Sulfate
330 Sulfuric Acid
127 Sodium Chlorate
Treatment
276 $Ca(OH)_2$
Solid Residue
507 $CaSO_4$
25 $Fe_4(Fe(CN)_6)_3$
190 Fe_2O_3
32 $Fe(OH)_2$
Liquid Effluent
Water +
70 NaCl
1016 Na_2SO_4
300 $(NH_4)_2SO_4$

Figure 12. Iron blue manufacture

$$FeSO_4 + (NH_4)_2\ SO_4 + Na_4\ Fe(CN)_6 \xrightarrow[\Delta]{} Fe(NH_4)_2\ Fe(CN)_6 + 2\ Na_2\ SO_4$$

and

$$6\ Fe(NH_4)_2\ Fe(CN)_6 + NaClO_3 + 3\ H_2SO_4 \longrightarrow 6\ Fe(NH_4)\ Fe(CN)_6 + 3\ (NH_4)_2\ SO_4 + 3\ H_2O + NaCl$$

The final product, ferric ammonium ferrocyanide or iron blue, is filtered, washed, dried, ground, and packaged. The so-called "soluble blues" are in reality colloidal dispersions in water and are made by peptization of iron blue with oxalic acid.

Much is known of production data for iron blue but little of the capacity. At present the market is of the order of 8 million pounds annually but in the past as much as 12 million pounds were manufactured domestically. Excess capacity will probably exist for the near future.

Approximately one-third of total iron blue consumption is due to importation and resale. The economics are favorable for importation, $0.38/lb versus $0.65/lb for domestically produced iron blue.

Waste management problems hinge on solids disposal since approximately 0.75 lb are produced per pound of iron blue. These wastes are most likely disposed of by landfill. The liquid effluent contains ammonium sulfate and sodium sulfate primarily. It appears that recovery of ferrous and sulfate values would be possible but probably not economically desirable since these chemicals are low cost items.

HEAVY METAL CYANIDES

Less is known of the manufacture of these compounds than any other cyanide class. Production, capacity, and capital value data are completely lacking. Further, companies such as C. P. Chemicals, Inc., and E. I. du Pont de Nemours and Company are very reluctant to discuss their operations. Table 20 describes various processes for making heavy metal cyanides.

According to E. I. du Pont de Nemours and Company, cyanide wastes are currently and historically have been mixed with large excesses of calcium hypochlorite in the manufacturing plant process sanitary sewer prior to discharge to the City of Niagara Falls treatment plant. Plant pretreatment facilities to prepare heavy metal cyanide wastes for final treatment by the City of Niagara Falls will be in operation by December 1976, but details are lacking.

Table 20. MANUFACTURING PROCESSES FOR HEAVY METAL CYANIDES

Cyanide	Process description
CuCN	Continuous chlorination with direct precipitation of CuCN from copper chloride and a cyanide. Recovery of cyanogen chloride for organic synthesis purposes.[a]
$Na\ Cu(CN)_2$ $K\ Cu(CN)_2$	Dissolve CuCN in NaCN or KCN solution; evaporate and collect crystals.[a]
$Zu\ (CN)_2$	Direct precipitation from zinc sulfate and sodium cyanide with evaporation and crystallization.[a]
$K\ Au(CN)_2$	Dissolve gold anodically in solution of KCN. Cathode compartment contains KOH.[b]
Ag CN	Direct precipitation with cyanide.[b]

---

[a] E. I. du Pont de Nemours and Company.

[b] Ref. 6.

TRANSPORTATION RATES AND REGULATIONS

The regulations regarding the shipment of inorganic cyanides are detailed in the Code of Federal Regulations.[7] These regulations detail packaging, labeling and classification of materials to be shipped. Table 21 lists the class and labeling requirements for some of the inorganic cyanides. The responsibility of proper packaging and labeling of articles for shipment lies with the shipper.

Table 22 shows typical charges for shipment of goods from Chicago to Kansas City by motor carrier. The low rate shown is most likely a commodity rate, which may not apply depending on amount and regularity of shipments. Table 23 gives typical shipping charges for shipment from Chicago to Kansas City by rail. This example was chosen since E. I. du Pont de Nemours and Company has a large distribution facility in Chicago.

Air transportation rates were not determined, as they are of little consequence. Barge rates were not determined but should be comparable to rail rates.

Table 21. REGULATIONS FOR SHIPMENT OF CYANIDES[7/]

Cyanide	Form	Class	Required label
Hydrogen cyanide, stabilized	liquid, solution > 5%	Poison A	Poisonous gas
Hydrogen cyanide, unstabilized	liquid	Unacceptable for shipment	
Hydrogen cyanide	solution ≤ 5%	Poison B	Poison
Sodium cyanide	solid, mixtures, solutions	Poison B	Poison
Potassium cyanide	solid, mixtures, solutions	Poison B	Poison
Calcium cyanide	solid, mixtures, solutions	Poison B	Poison
Copper, zinc, lead, or silver cyanides	solid, mixtures, solutions	Poison B	Poison
Ferrocyanide	solid, mixtures, solutions	-	-
Ferricyanide	solid, mixtures, solutions	-	-

Table 22. MOTOR CARRIER SHIPPING CHARGES, CHICAGO TO KANSAS CITY[a]

Weight range	Shipping charges ($/100 lb) Low	High
Minimum:	13.40	
< 500	7.37	9.63
500-1,000	6.36	8.61
1,000-2,000	5.50	7.52
2,000-5,000	5.08	7.11
5,000-24,000	4.14	5.77
24,000 and up	2.01	2.72

---

[a] Distance is about 500 miles.
Source: Consolidated Freightways, Yellow Freight System, Inc.

Table 23. RAIL CARRIER SHIPPING CHARGES, CHICAGO TO KANSAS CITY[a]

Weight range	Shipping charges ($/100 lb)
20,000-30,000	2.29
30,000-40,000	1.75
40,000-50,000	1.44
50,000-60,000	1.37
60,000-80,000	1.22
80,000 and up	1.14

---

[a] Distance is about 500 miles.
Source: Illinois Central Gulf Railroad.

It should be noted that cyanide transportation rates do not differ from rates for other goods because of their toxicity. Essentially all commodities may be shipped from one point to another at the same rate for each type of carrier. The carrier, however, may be regulated as to what other goods may be shipped along with cyanides in the same load.

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CHAPTER VII

AREAS OF UTILIZATION

The use of cyanides by industry, mining, and agriculture is discussed under separate headings of this chapter. Each usage involves a unique set of circumstances or parameters, and no overall generalizations can be drawn as to the usage rate or the future of cyanides. For this reason each application is individually described, and details as to the growth rate over the years 1965 to 1975 are given together with a comment on the future cyanide usage to 1985. The percentage of total cyanide usage as NaCN equivalent for each sector is given by the headings.

METAL FINISHING (62.5%)

Sodium, potassium, and various heavy metal cyanides are used extensively in metal finishing operations. In fact, this industrial sector constitutes the largest single use of cyanides other than for organic synthesis purposes, which lie outside the scope of this report.

The metal finishing industrial sector is very large, geographically diffuse, and largely unknown in the distribution and magnitudes of the numbers of captive, semicaptive, and independent job shops. Estimates by industry sources of the number of metal finishing shops range from 15,000 to 60,000 or even 80,000 establishments.[1/] Of these, there are perhaps 5,000 to 20,000 electroplating operations, of which approximately 75% utilize cyanides in one or more plating lines. The sizes of the establishments range from shops employing fewer than 10 persons to captive shops employing approximately 500 operators.

The 1972 Census of Manufactures indicates some 3,265 establishments in the SIC 3471 - Plating and Polishing category.[2/] The number of employees is approximately 55,000, with a payroll of over $400 million. This estimate of 3,265 plating shops differs considerably from those above by industry sources. The high estimates have been suggested by private individuals and trade and professional associations such as the National Association of Metal Finishers, the Metal Finishing Suppliers' Association, and the American Electroplaters' Society. The differences among the various estimates are due to the difficulty of locating an electroplating operation within a company. For example, the Census of Manufactures may locate a luggage manufacturer in Denver and identify the company as belonging in SIC 3161 - Luggage Manufacturing category, but would not classify the company in SIC 3471 - Plating and Polishing. On the other hand, a luggage hardware manufacturer SIC 3429 Cutlery, Hand Tools, and General Hardware (including luggage hardware and cartop racks) might be included in the Plating and Polishing category as well, since the plating operation is one of the few principal steps in the manufacturing process. No one individual, organization, or agency knows even approximately the number of plating operations and establishments in the U.S.; or what fraction of these locations utilize cyanides. Further, a cyanide plating line may be placed in operation or taken out of operation at any time with a very short turnaround time.

The term "metal finishing" includes a multitude of operations, but cyanides are employed principally in electroplating, metal cleaning, and to a much smaller extent in metal stripping. "Electroplating" refers to the electrochemical process by which a conductive substrate receives a metal coating or layer from an appropriate solution for the purposes of protecting, altering, and/or enhancing the substrate surfaces. "Metal stripping" refers to chemical removal of a previously deposited metal layer by immersion in an appropriate solution, often containing cyanide.

Much has been written on the subject of electroplating and metal stripping, including several EPA documents for the development of effluent guidelines for the electroplating industry. The references at the end of this section include some of the principal sources of information, but are not intended to be an exhaustive compilation. Cyanides as the sodium, potassium, cadmium, zinc, copper, silver, and gold salts are used in electroplating of cadmium, zinc, copper, silver, gold, brass, and bronze.

Cadmium

Electrodeposits of cadmium are used extensively to protect steel and cast iron against corrosion. Most cadmium plating is done in cyanide baths made by dissolving cadmium cyanide or cadmium oxide in a caustic sodium cyanide solution. Brighteners include aldehydes, ketones, alcohols, dextrin, etc., plus proprietary materials obtainable from various metal finishing materials companies. The anodes for cadmium plating usually consist of ballshaped cadmium metal held in a bare steel cage. Typical bath compositions for cadmium electroplating are given in Table 24.

Table 24. CYANIDE CADMIUM ELECTROPLATING BATH COMPOSITIONS[3/]

Solution	Ratio of total sodium cyanide to cadmium metal	Composition (oz/gal)				
		CdO	Cd metal	NaCN	NaOH	Na_2CO_3
1	4 to 1	3.00	2.62	10.4	1.90	4.0 to 10.0
2	7 to 1	3.00	2.62	18.4	1.90	4.0 to 6.0
3	5 to 1	3.50	3.06	15.3	2.10	4.0 to 8.0
4	4.5 to 1	5.50	4.82	21.7	3.44	4.0 to 6.0

Note: Solution 1 - for use in still tanks and bright barrel plating.
Solution 2 - for use in still tanks and automatic plating. Not for use in barrel plating.
Solution 3 - for use in still tanks, automatic plating, and barrel plating.
Solution 4 - for plating cast iron; high-speed.

Sodium carbonate forms in the bath because of slow decomposition of cyanide and general absorption of carbon dioxide from the air. In addition, oxygen released by insoluble or polarized anodes decomposes cyanide and one of the products is carbonate. Excessive buildup of sodium carbonate can result in anode polarization and irregular, dull deposits. The simplest method of carbonate removal is by "freezing," i.e., cooling the bath to slightly below 15°C for about 24 hr, after which the bath is decanted from the solid sodium carbonate. Calcium sulfate or cyanide may be used to form calcium carbonate as a bulky precipitate.

Solutions for chemically stripping cadmium plat are composed of ammonium nitrate, ammonium persulfate, and ammonium hydroxide, and other materials. Electrolytic stripping is accomplished by making the substrate to be stripped anodic and immersing it in a solution of caustic sodium cyanide. Compositions of various cadmium stripping solutions are given in Table 25.

Zinc

Zinc plating is often preferred for coating ferrous parts for protection against atmospheric corrosion because it is relatively cheap and redily applied in barrel, tank, or continuous plating facilities. It is estimated that zinc deposition accounts for approximately 80% of all cyanide plating performed today.[1/] Typical zinc bath compositions are given in Table 26.

Table 25. SOLUTIONS FOR STRIPPING ELECTROPLATED CADMIUM[3/]

Solution	Composition (oz/gal)	Immersion time (min)
1	Ammonium nitrate (14-18)	10-20
2	Hydrochloric acid (22° Be), undiluted Antimony trioxide (2)	10-20
3	Chromic acid (27) Sulfuric acid (95%) (6.4 fluid oz.)	5-10
4	Ammonium persulfate (6.7) Ammonium hydroxide (13 fluid oz.)	5-10
5	Sodium cyanide (8-12) Sodium hydroxide (2-4)	10-20

Note: Solutions listed in order of preference. Immersion times are for removal of deposits 0.3-0.5 mil thick. Solution 5 for electrolytic stripping at 50-100 amp/sq ft and 6-8 volts, room temperature.

Table 26. CYANIDE ZINC PLATING BATH COMPOSITIONS[3]

Solution	Ratio of total sodium cyanide to zinc	Composition (oz/gal) Zn(CN)2	NaCN	NaOH	Sodium Polysulfide
1	2.7-3.0 to 1	8-11	5.2-8.8	10-12	0.2
2	2.5-3.0 to 1	8-11	4.3-8.8	10-12	0.2
3	2.0-2.5 to 1	8-12	2.1-6.5	10-12	0.2
4	2.7 to 1	5.6	12.3	5.0	0.2
5	2.3 to 1	7.5	14.0	7.4	0.2

Note: Total sodium cyanide equals the sum of the sodium cyanide and the sodium cyanide equivalent of the zinc cyanide or the zinc metal equivalent in zinc oxide.
Solutions 1 and 5 are used for barrel plating.
Solutions 2 and 4 are used for still tank plating.
Solution 3 is used for conduit tubing and strip plating.
Solutions 4 and 5 utilize zinc oxide instead of zinc cyanide.

Brighteners for zinc cyanide plating include dextrin, pyrogallol, gum arabic, etc., and proprietary materials. Zinc anodes in the form of balls or elliptical bars are often used and held in a spiral steel cage. Insoluble steel anodes are also employed.

Zinc metal may be chemically or electrochemically stripped. Table 27 presents a typical bath composition for electrochemically stripping zinc. Chemical stripping baths do not contain cyanide.

Copper

Copper plating is widely performed in electroforming, plating on zinc die-castings, leaded brass, as stop-offs, for heat transfer, etc. Typical bath compositions for copper electroplating are given in Table 28.

Proprietary additives are essential in the high concentration plating baths (Solutions 5 and 6 of Table 28) in order to prevent pitting and guarantee brightness of the deposits. The potassium complexes formed by the combination of potassium ion and copper cyanide are more soluble

Table 27. SOLUTION FOR ELECTROCHEMICALLY STRIPPING ZINC[3/]

Composition (oz/gal)		
NaCN	NaOH	Immersion time (min)
8-12	2-4	5-10

Note: Immersion time for stripping deposits 0.2 to 0.3 mil thick. Anodic condition at 50-100 amp/sq ft at 6-8 volts, room temperature.

Table 28. CYANIDE COPPER PLATING BATH COMPOSITIONS[3/]

Solution	Ratio of copper to free cyanide	Composition (oz/gal)					
		CuCN	NaCN	Na_2CO_3	NaOH	KOH	Rochelle salt
1	2.1 to 1.0	3.0	4.5	2.0	To pH 12.0-12.6	-	-
2	1.75 to 1.0	6.0	9.0	-		1.0-2.0	6.0-10.0
3	3.10 to 1.0	3.5	4.6	4.0	To pH 12.0-12.6	-	6.0
4	2.0 to 1.0	6.0	7.0	8.0	To pH 13.0	-	12.0
5	2.3 tc 1.0	16.0	18.0	2.0	4.0 ($pH > 13.0$)	-	-
6	5.6 to 1.0	8.0	12.5	2.0	-	5.6 ($pH > 13.0$)	-

Note: Solution 1 is a dilute cyanide bath for strike coating.
Solution 2 is a standard barrel plating solution.
Solution 3 is used for copper strikes.
Solution 4 is used for plating up to about 0.3 mil thickness.
Solutions 5 and 6 are used for producing deposits of 0.3 to 2.0 mils thick.

than those formed with sodium ion. Hence, higher metal contents and higher deposition rates are possible. In addition, the potassium bath has a more flexible set of operating characteristics and permits a higher current density with less danger of "burning" the deposits.

Additives for copper baths include gelatin, glue, glycine, etc., which result in smoother and finer-grained deposits. Some brighteners are proprietary formulations.

High-purity copper anodes are recommended for use in high-efficiency baths. Steel anodes are often used with the dilute cyanide baths. Often a film of cuprous oxide, or occasionally cupric oxide, is formed during electrolysis. When this happens, the anodes must be removed and cleaned. Anode bags of cotton or nylon or diaphragm systems have been used to prevent migration of anode particles to the cathode with resultant roughness to the copper deposit.

Brass and Bronze

Brass and bronze plating principally refers to the electrodeposition of alloy coatings containing copper and zinc, and copper and tin, respectively. Proportions of these alloys included in major commercial applications are listed in Table 29.

Table 29. APPROXIMATE COMPOSITION OF MAJOR COMMERCIAL COPPER AND ZINC AND COPPER AND TIN ALLOYS[3]

Alloy	Approximate composition (%) Copper	Zinc	Tin
Brass	70	30	-
White-Brass	30	70	-
Bronze-Brass	90	10	-
Tin-Bronze	85-90	-	10-15
Speculum metal (brass)	55-60	-	40-45

Of these alloys, the conventional brass formulation, 70-30 copper-zinc, and the tin-bronze formulations are the most important.

Brass plate is deposited for decorative purposes, e.g., various hardware and electrical fittings. The deposit is also used to promote adhesion of rubber to steel and other metals. Typical brass plating bath compositions are given in Table 30.

Table 30. CYANIDE BRASS PLATING BATH COMPOSITIONS[3/]

Solution	pH	Composition (oz/gal)									
		CuCN	$Zn(CN)_2$	NaCN	KCN	Na_2CO_3	K_2CO_3	NH_3	NaOH	KOH	Rochelle salt	NaSCN
1	10-11	3.5-4.2	1.2-1.5	6.0-8.0	-	4.0	-	0.1-0.4	-	-	-	-
2	-	5.4	1.6	1.6	-	-	-	-	-	-	-	-
3	-	9.4-14.1	0.4-1.2	12.0-18.0	-	-	-	-	6.0-10.0	-	-	-
4	12	13.4	2.4	20.1	-	-	-	-	1.5	-	-	-
5	13	5.9	2.3	-	16.8	-	4.0	-	-	2.0	-	1.5
6	10-11	7.0	3.6	12.0	-	4.0	-	0.7-1.6	-	-	6.0	-

Note: Solutions 1 and 2 are conventional baths, low current density, < 10 amp/sq ft.
Solutions 3 through 6 are high speed plating baths with current densities up to 160 amp/sq ft.
The NH_3 is added as a 28% solution in fluid ounce.

The high-speed baths operate from 5 to 160 amp/sq ft, but more generally in the range 20-40 amp/sq ft. The increased rates are possible due to an increase in metal content, substitution of potassium for sodium cyanide, an increase in pH by the addition of sodium or potassium hydroxide, the addition of Rochelle salt, and higher bath temperatures.

Organic brighteners such as thiourea and piperonal are often added. Antipitting agents of a proprietary origin are available. A small quantity of ammonia has been found to improve appearance and brightness of the brass deposit.

The composition of the anodes should be nearly the same as that of the desired deposit, since anode corrosion occurs during electrolysis and could change the bath composition.

Bronze plating is commercially important as a decorative and protective finish on various kinds of hardware and steel wire products. Bronze is employed as a stop-off in gas nitriding of steel, for "building up" or restoring worn or undersized parts, and as a coating on bearings. Bronze plate is occasionally a substitute for nickel plate and can serve as a basis metal for subsequent plating by chromium or nickel.

Typical bronze plating bath compositions are given in Table 31.

Proprietary brighteners for bronze plating baths are available. Bronze anodes can be used, but should not contain more than 12% tin. A preferred variation is to use copper anodes and add the tin compounds as needed for bath maintenance.

Stripping of electroplated bronze is accomplished by caustic cyanide solution or by ammonium persulfate in an ammonia solution.

Silver

Various silver plating baths are available for industrial uses, including aircraft engine bearings, electronics applications, jewelry, silverware, etc. Silverplate may vary from less than 1 mil to 1/4 in. in thickness depending on the application. Cyanide plating bath compositions are given in Table 32.

A silver strike is generally performed first in order to prevent the formation of loosely adhering deposits. Strike solutions have relatively low silver content and a high cyanide concentration.

Table 31. CYANIDE BRONZE PLATING BATH COMPOSITIONS[3]

Solution	pH	Composition (oz/gal) CuCN	$Na_2SnO_3 \cdot 3H_2O$	NaCN	NaOH	Rochelle salt	Tin deposit (%)
1	12.6	4.7	5.1	7.2	1.0	-	10
2	-	3.9	4.7	8.6	1.3	6.0	12
3	13	5.4	2.7	8.7	1.0	-	15
4	-	2.0	2.0	6.0	1.0	-	16

Note: All baths are operated from 20 to 100 amps/sq ft. Solution 2 uses potassium salts rather than sodium salts and the values given are for potassium salts.

Table 32. CYANIDE SILVER PLATING COMPOSITIONS[3/]

	Composition (oz/gal)						
Solution	AgCN	NaCN	Na_2CO_3	KCN	K_2CO_3	KNO_3	KOH
1	0.1-0.2	5-8	-	-	-	-	-
2	0.5-0.7	8-12	1.2	-	-	-	-
3	3.3-4.4	-	-	4-6	3-12	-	-
4	6.0-7.3	-	-	6.0-7.3	3.0-10.7	3.0-12.0	0.4-1.6

Note: Solutions 1 and 2 are for silver strikes on nickel plated steel and nonferrous metals, respectively. Solution 3 is a conventional cyanide silver bath. Solution 4 is a high speed, high efficiency bath. The pH is not controlled in any of the above baths.

Striking time and voltage must be controlled since prolonged application can produce a powdery, loosely adhering deposit, thus defeating the purpose of the strike. After striking, the conventional or high-speed baths are used.

Various sulfur compounds, carbon disulfide or ammonium thiosulfate, are sometimes added to insure deposit smoothness and brightness. Other proprietary additives are available to increase plate hardness, tarnish-resistance, and brightness. The additives may contain selenium, antimony, or lead in conjunction with wetting agents, and sulfur compounds.

Anodes may be of silver or stainless steel. In the first case, operation of the bath will cause the silver content to rapidly increase beyond the normal limits at which point the excess silver must be removed by electrolysis, using a steel anode. In the second case, the silver content falls and must be replenished.

Gold

Gold plating is industrially important in the areas of electronics applications and in jewelry. It is ideal for electronics applications because of resistance to tarnishing and corrosion, low electrical contact resistance and ease of soldering.

Typical gold plating bath compositions are given in Table 33.

Table 33. CYANIDE GOLD PLATING BATH COMPOSITIONS3/

Solution	Composition (oz/gal) Au (troy oz.)	KCN	K_2HPO_4	K_2CO_3	$K_4Fe(CN)_6$
1	0.25	2	2	-	-
2	0.125	0.01-2.0	2	-	-
3	1.0	2.7	2.7	2.7	-
4	0.5	4.0	4.0	4.0	-
5	2.7	-	-	-	27

Note: Solution 1 - for flash and alloy plating.
Solution 2 - for flash and gold alloy plating of jewelry.
Solution 3 - for thick plate (0.05-1.0 mil).
Solution 4 - for barrel plating.
Solution 5 - for high efficiency, high-speed plating (deposits 1.0 mil in 30 min).
pH maintained between 10.5 and 11.8.

The metal content is furnished by complex sodium or potassium gold cyanides, $Na(K)Au(CN)_2$. Soluble anodes are rarely used. Gold is added routinely as the cyanide salt. The potassium salts are preferred for the high efficiency, high concentration solutions because they are more soluble than the corresponding sodium salts.

Insoluble anodes may be of stainless steel, platinum-clad tantalum, platinum plated titanium, or carbon rods.

Gold stripping can be accomplished by anodic oxidation in a warm cyanide solution containing a small amount of hydrogen peroxide as a catalyst. Other solutions not requiring electrolysis consist of 5% potassium cyanide and sufficient amounts of 30% hydrogen peroxide to cause dissolution. The latter solution can be dangerous if too much peroxide is used since it can act on the cyanide ion as well, releasing large volumes of gases.

Chemical Consumption

The previous detailed listing of various cyanide plating bath compositions permits a number of important points to be developed regarding cyanide consumption. Heavy reliance is made on sodium cyanide as a complexing agent for metals. Only in relatively rare cases is the more expensive potassium cyanide used for its superior solubility properties in the formulation of high-speed plating baths. The cost difference is substantial, amounting to nearly 56% more at October 1975 prices. Further, since cyanide atmospheric oxidation in the bath occurs slowly and continually, the added cyanide salts for replenishment become a significant cost factor over the long run. It is estimated that approximately one-half of cyanide consumption is due to oxidation of cyanide ion and one-half is lost by drag-out as work pieces are removed from the plating solution.[1]

Plating baths are generally purchased from a metal finishing supplier as a complete bath only once for startup. Beyond this point, and excluding the rare occasions of bath disposal because of irreversible contamination, bath replenishment is accomplished by additions of sodium cyanide (or potassium cyanide) and the metal cyanide as salts when plating with insoluble anodes. Small additions of the metal cyanide salt may be made infrequently to adjust the solution composition balance.

Except for gold plating baths, platers generally buy raw chemicals and formulate the plating bath themselves. Proprietary brighteners and levelers to insure uniform metal deposits are purchased only when required. Metal finishers purchase proprietary formulations for brighteners mainly. Sodium cyanide is conveniently purchased and handled in 100 lb drums.

Metal Finishing Suppliers

The major suppliers of cyanide salts and proprietary plating baths and chemical formulations are given in Tables 9 (Chapter V) and 34, respectively.

Outlook for Cyanides in Metal Finishing

Various industry sources have been contacted regarding the future of cyanides in metal finishing. A general consensus has emerged which indicates that cyanide usage has declined over the last 5 years but has stabilized at least temporarily as electroplaters adopt a wait-and-see attitude regarding effluent restrictions.

Table 34. MAJOR COMPANIES SUPPLYING PROPRIETARY PLATING BATHS AND CHEMICAL FORMULATIONS TO THE METAL FINISHING INDUSTRY

Company	Location
Udylite Corporation	Warren, Michigan
Sel-Rex Corporation	Nutley, New Jersey
Du Tone Corporation	Waukegan, Illinois
Mac Dermid, Inc.	Waterbury, Connecticut
Lea-Ronal, Inc.	Freeport, New York
R. O. Hull and Company, Inc.	Cleveland, Ohio
C. P. Chemicals, Inc.	Sewaren, New Jersey
M&T Chemicals, Inc.	Rahway, New Jersey
Technic, Inc.	Providence, Rhode Island
Enthone, Inc.	New Haven, Connecticut
E. I. du Pont de Nemours and Company, Inc.	Wilmington, Delaware
Allied Research Products, Inc.	Baltimore, Maryland
Aldoa Company	Detroit, Michigan
Engelhard Industries, Inc.	Murray Hill, New Jersey
The 3M Company	St. Paul, Minnesota
Enquist Chemical Company, Inc.	Brooklyn, New York
Frederick Gumm Chemical Company, Inc.	Kearny, New Jersey

Three pieces of evidence are offered to substantiate this viewpoint:

1. No recent major facility expansions have occurred.

2. A definite shift to the use of low cyanide or noncyanide plating baths has occurred, particularly for zinc processes. This trend is discussed more fully in Chapter IX.

3. Approximately 70% of the small plating shops have switched to noncyanide baths.[1]

On balance MRI forecasts cyanide consumption in the metal finishing sector to decrease by at least 25% over the next 10 years, but that a substantial amount of cyanide, principally NaCN, will continue to be used as it has been historically. The estimated NaCN equivalent consumption for 1975 to 1985 is given in Table 35.

Table 35. NaCN EQUIVALENT CONSUMPTION IN METAL FINISHING IN 1975-1985

Year	Estimated usage (million lb)
1975	50
1980	43.8
1985	37.5

In the absence of an expanding economy the drop in cyanide consumption might be more dramatic. However, as the economy expands and affects the amount of metal processed, the larger metal finishing shops will probably continue to use cyanides, with the smaller shops completely shifting to noncyanide systems.

PIGMENT (IRON BLUE) (16.9%)

In the past, iron blue, ferric ammonium ferrocyanide [$Fe(NH_4)Fe(CN)_6$] has been widely used as a pigment in paints, enamels, lacquers, inks, carbon paper, typewriter ribbons, crayons, linoleum, composition tile, blueprint paper, laundry blues, plastics, chemical coatings, etc. The previous listing was true in 1965 but is not accurate today.[1] Iron blue is no longer an important pigment in consumer household paint, crayons, linoleum, composition tile, etc. The major uses are now as pigment for various types of inks, carbon papers, and for coloration of plastics. A small amount of iron blue is used in industrial paints, e.g., safety paint.

The reason for the decline in the general area of consumer paint is due to the characteristic color instability of iron blue in alkaline media. The trend in consumer paints is to latex water-based paints which are moderately alkaline. Iron blue is simply incompatible as a pigment in such a system. Special alkali-resistant, high purity grades of iron blue are sometimes available, but their cost is relatively high, the supply is scarce and uncertain, and the long-term stability is not enough improved to warrant continued use in alkaline media.

One paint manufacturer in Kansas City, Missouri, offered consumption figures for iron blue listed in Table 36.[2]

Table 36. ANNUAL CONSUMPTION OF IRON BLUE
OF A KANSAS CITY PAINT MANUFACTURER,
1971-1975

Year	Pounds of iron blue consumed
1971	2,000
1972	800
1973	180
1974	147
1975 (8 months)	36

The products currently using iron blue amounted to only 600 gal. in 1975 and were special paints for industrial use, e.g., safety paint and other enamels requiring bright, deep blue colors which are durable. Other paint manufacturers contacted indicated that usage of iron blue is rapidly decreasing on an industry wide basis.

The only significant usage of iron blue is in paints and enamels having special industrial product applications, e.g., safety signs, farm implements, trucks, tractors, etc. For these uses, there are no organic or inorganic pigments with suitable durability and economics to replace iron blue. Little change in the use of iron blue for these applications is anticipated in the future.

Large amounts of iron blue were also used in the manufacture of chrome green for paint pigment, the latter being a mixture of chrome yellow and iron blue.[3] However, chrome yellow contains lead and chromium. These elements have been tagged as being ecologically undesirable and a health hazard. Again, the iron blue market in nearly all paints, enamels, and lacquers has decreased to a very low level and accounts for much less than 5% of the total iron blue consumption by industry.[4]

Iron blue has been used in art materials, paints, and crayons because of its extremely high tinctorial power. However, it has been replaced by copper phthalocyanine blue, an organic pigment of high tinting strength and excellent heat and oxidation resistance. Further, a major manufacturer of floor tiles in Lancaster, Pennsylvania, indicated that any future use of iron blue in this sector is negligible. The markets for iron blue are rapidly decreasing as organic pigments having greater oxidation resistance are developed.

The current major uses of iron blue are in the formulation of various types of inks for carbon paper, printing, and typewriter ribbons. According to one industry spokesman, the market for iron blue is divided in the manner indicated in Table 37.

Table 37. CONSUMPTION OF IRON BLUE BY MARKET USE IN 1975[4]

Usage	Iron blue consumption in 1975	
	Approximate % of market	Approximate consumption (million lb)
Printing ink (including publishing gravure inks and typewriter ribbons)	45	5.5
Carbon paper ink (including one-time and multiple-copy types)	35	4.5
Coloration of plastics, especially polyethylene	10	1.5
All other uses, including paint, enamels, papermaking and as an anti-caking agent	10	1.5
Total	100	13.0

All printing ink contains a small amount of iron blue, typically 2 to 10% iron blue plus other pigments including carbon black, the principal material. Carbon paper ink may contain 10 to 25% iron blue plus other pigments. Iron blue is the lowest priced blue pigment acceptable for these applications.

There are approximately 350 domestic ink manufacturers of which six firms may account for 60 to 70% of the total printing ink manufactured according to one estimate. The major manufacturers of printing ink are listed in Table 38.

The value of iron blue pigment in ink in 1972 amounted to $3.5 million and the value of ink (retail sales) amounted to $4.25 million. Temple Patton estimated some 9 million pounds of iron blue were consumed in ink manufacture in 1972.[5]

Table 38. CURRENT MAJOR INK MANUFACTURERS IN ORDER OF BUSINESS VOLUMES

Company	Location
IPI Printing Inks Division of Inmont Corporation	New York, New York
Sinclair and Valentine Company Division of Wheelabrator-Frye, Inc.	New York, New York
General Printing Ink Division of Sun Chemical Corporation	New York, New York
Flint Ink Corporation[a]	Detroit, Michigan
Borden Chemical Company[b] Division of Borden, Inc.	Columbus, Ohio
Sleight and Hellmuth, Inc.	Chicago, Illinois
Acme Printing Company, Inc.	Chicago, Illinois

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[a] Merged with Cal/Ink Division of Tenneco, Inc., San Francisco, California.

[b] Merged with Levey Division, Cities Service Company, Inc., Cincinnati, Ohio.

Source: MRI estimates.

The ink manufacturers serve a vast and diffuse market. It has been estimated that the size distribution of printing establishments in 1972 was that as listed in Table 39.

Table 39. SIZE CLASSIFICATION OF PRINTING ESTABLISHMENTS IN 1972[5]

Size classification	Approximate number of shops
Small (< 50 employees)	18,000
Medium (50-250 employees)	850
Large (> 250 employees)	150
Total	19,000

The printing establishments include all printing and publishing facilities, e.g., newspapers, periodicals, books, commercial, business forms, etc.

The recent historical growth (1955 to 1972) of the printing ink industry averaged 5 to 6%/year and is expected to continue in the near future.[6/] This growth is related to the growth in the entire communications field and could be even greater over the next 10 years.

Three segments of the printing ink industry showing the most growth in recent years are:

Lithographic ink - printing from a planar surface

Flexographic ink - printing from raised type

Rotogravure ink - printing from a recessed or engraved type

All these techniques are used for publications, packaging and labels. These ink types accounted for approximately 45% of all printing ink produced in 1972. Growth rates for the three segments as a group averaged 10% per year from 1963 to 1972 with a growth rate of nearly 15% for the lithographic sector.[5/]

Carbon paper is a general term describing a paper coated with hardened ink and used for duplicating purposes. A distinction may be made between one-time, pencil, and typewriter carbon papers, and the applications range from single use, to sales books, to maximum repeat requirements. Performance depends in part on the ink composition of which iron blue is a prominent pigment.

Growth in this field has been related to growth of the entire communications and business areas and has been approximately 5%/year over the last 10 years. Recently, carbonless paper has become available which contains organic dyes as microencapsulated color agents. Future iron blue consumption in the carbon paper ink area is estimated to decrease as organic carbonless paper becomes more prominent.

Finally, iron blue is used as a colorant for polyethylene and other plastics. The principal application appears to be the manufacture of green refuse bags. This market is significant but small and accounts for approximately 0.5 million pounds of iron blue annually.

The overall growth of iron blue consumption is difficult to forecast because of individual rising and falling trends of the various industrial sectors. Industry spokesmen indicate slow growth over the next 10 years. Figure 5 of Chapter V illustrates total consumption of iron blue for a 2 and 4% annual increase. Growth is estimated to be 3% annually.

Environmental management of inks, dyes, and pigments containing iron blue is a difficult concept to apply in the case of iron blue. Certainly the two domestic manufacturers of iron blue, American Cyanamid Company and Hercules, Inc., are point sources worth monitoring. Data on iron blue manufacture are included in Chapter V in this report.

Processors utilizing iron blue as a pigment are more diffuse and as an industry segment are phasing out iron blue as a raw material, especially for paint. The six major ink manufacturers are potential point sources. When the final product, as carbon paper, ink or trash bags, is manufactured, distributed and consumed, the geographic factor coupled with the consumer dilution of the products, make environmental management difficult except at the municipal or county waste disposal areas. Since iron blue is nontoxic and harmless except perhaps when incinerated, there should be no danger to animal or plant life.

METAL AND MINERAL RECOVERY (8.2%)

Cyanides are used extensively in the extraction and beneficiation of metals and minerals in the United States. Cyanides are principally used (a) to extract gold and silver from ore, i.e., cyanidation; and (b) as a depressant in the selective flotation of copper, lead, zinc, and fluorspar ores.

Cyanidation

The use of cyanide to extract gold was introduced domestically in South Dakota in 1899.[1] Cyanidation currently is the single most important method of recovery for gold. In 1972, nearly 55% of the U.S. gold production resulted from cyanidation.[2]

Cyanidation is also a method of recovery for silver; however, very little silver is recovered by cyanidation domestically, except as a by-product of gold production. This discussion will be limited to gold production, with the understanding that silver is recovered as a by-product of cyanidation recovery of gold.

Process Descriptions - Five major operations currently recover gold by cyanidation, Table 40. Numerous other gold mining operations are in existence with the bulk of these recovering gold by various methods of gravity concentration; a few of these employ cyanidation on a small scale.

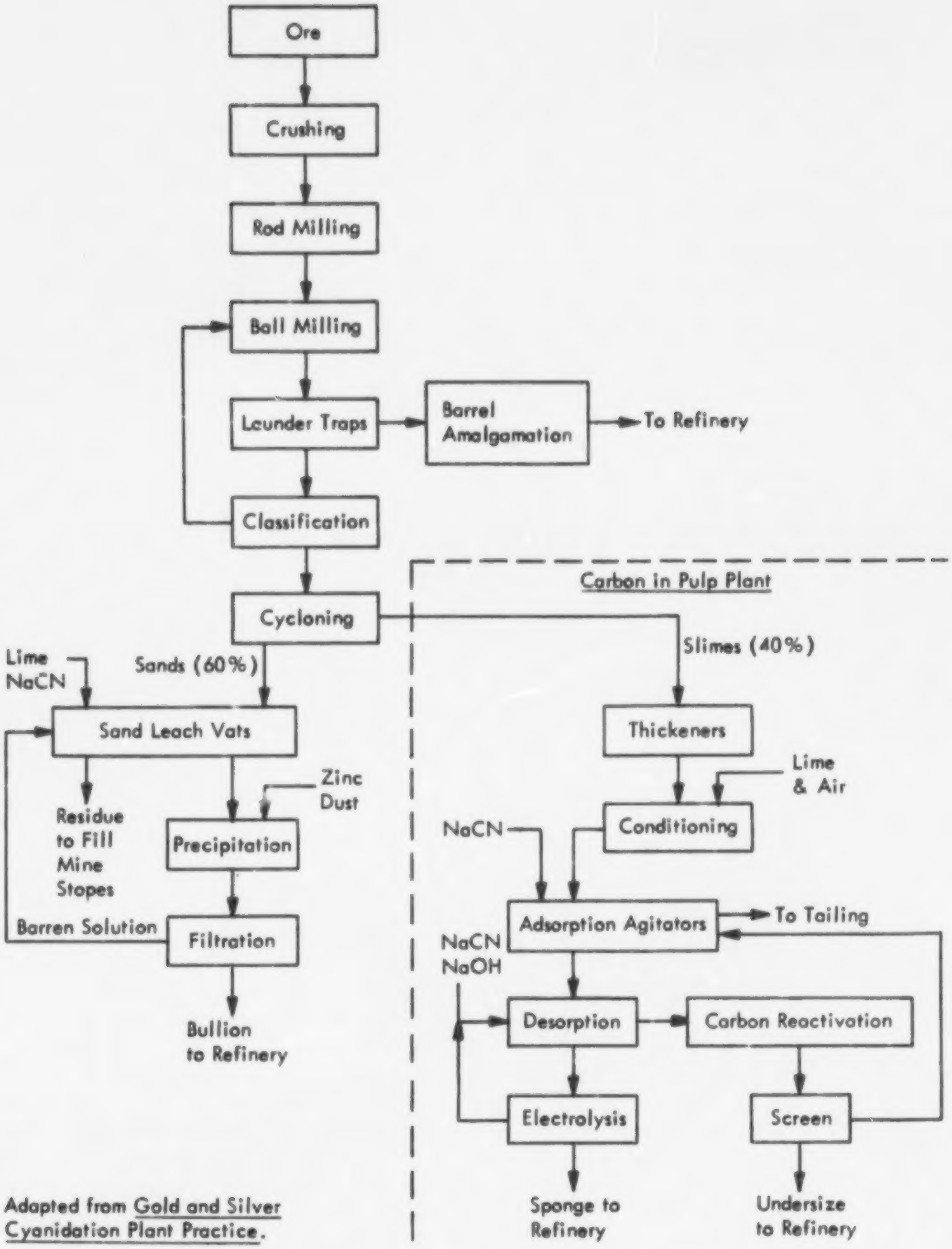
The Homestake Mining Company is the largest domestic producer of gold. A simplified description of the Homestake operation is shown in Figure 13.

Table 40. MAJOR OPERATIONS RECOVERING GOLD AND SILVER BY CYANIDATION[1]

Company	Location	Ore type	Mill capacity, tons/24 hr
Homestake Mining Company	Lead, South Dakota	Gold	5,600
Carlin Gold Mining Company	Carlin, Nevada	Gold	2,500
Cortez Gold Mines	Cortez, Nevada	Gold	2,400
Knob Hill Mines, Inc.	Republic, Washington	Gold-silver	250
Magma Copper Company, San Manuel Division	San Manuel, Arizona	Copper	12

The Homestake method is unique in that the sands and slimes are treated in separate cyanidation circuits. The sand portion is leached in vats by percolating alkaline sodium cyanide solution through the sands, and the gold is recovered by precipitation with zinc dust.

The slime portion is treated by the Bureau of Mines' developed carbon-in-pulp method. Carbon-in-pulp treatment at Homestake constitutes mixing the thickened slimes with 6 x 16 mesh activated coconut charcoal[1] in four agitated vats. The carbon and the pulp flow counter-currently and are separated between each vat by screening.


Ore
Crushing
Rod Milling
Ball Milling
Launder Traps
Barrel Amalgamation
To Refinery
Classification
Cycloning
Carbon in Pulp Plant
Sands (60%)
Slimes (40%)
Lime
NaCN
Sand Leach Vats
Thickeners
Lime & Air
Zinc Dust
Residue to Fill Mine Stopes
Precipitation
NaCN
Conditioning
Barren Solution
Filtration
Adsorption Agitators
To Tailing
NaCN
NaOH
Bullion to Refinery
Desorption
Carbon Reactivation
Electrolysis
Screen
Sponge to Refinery
Undersize to Refinery

Adapted from Gold and Silver Cyanidation Plant Practice.

Figure 13. Homestake process schematic

The gold is adsorbed by the carbon and then desorbed by leaching with hot sodium hydroxide-sodium cyanide solution. The gold-loaded caustic-cyanide solution is then electrolyzed, recovering the gold on stainless steel wool cathodes.[3] The caustic-cyanide solution is recycled; the desorbed carbon is reactivated by heat and is also recycled.

The Carlin Gold Mining Company is the second largest domestic gold mining operation and in 1972 the third largest producer of gold, behind Kennecott Copper Corporation's Utah copper mine. The Carlin venture is relatively recent with production started in 1965 and full-scale production reached in 1966.

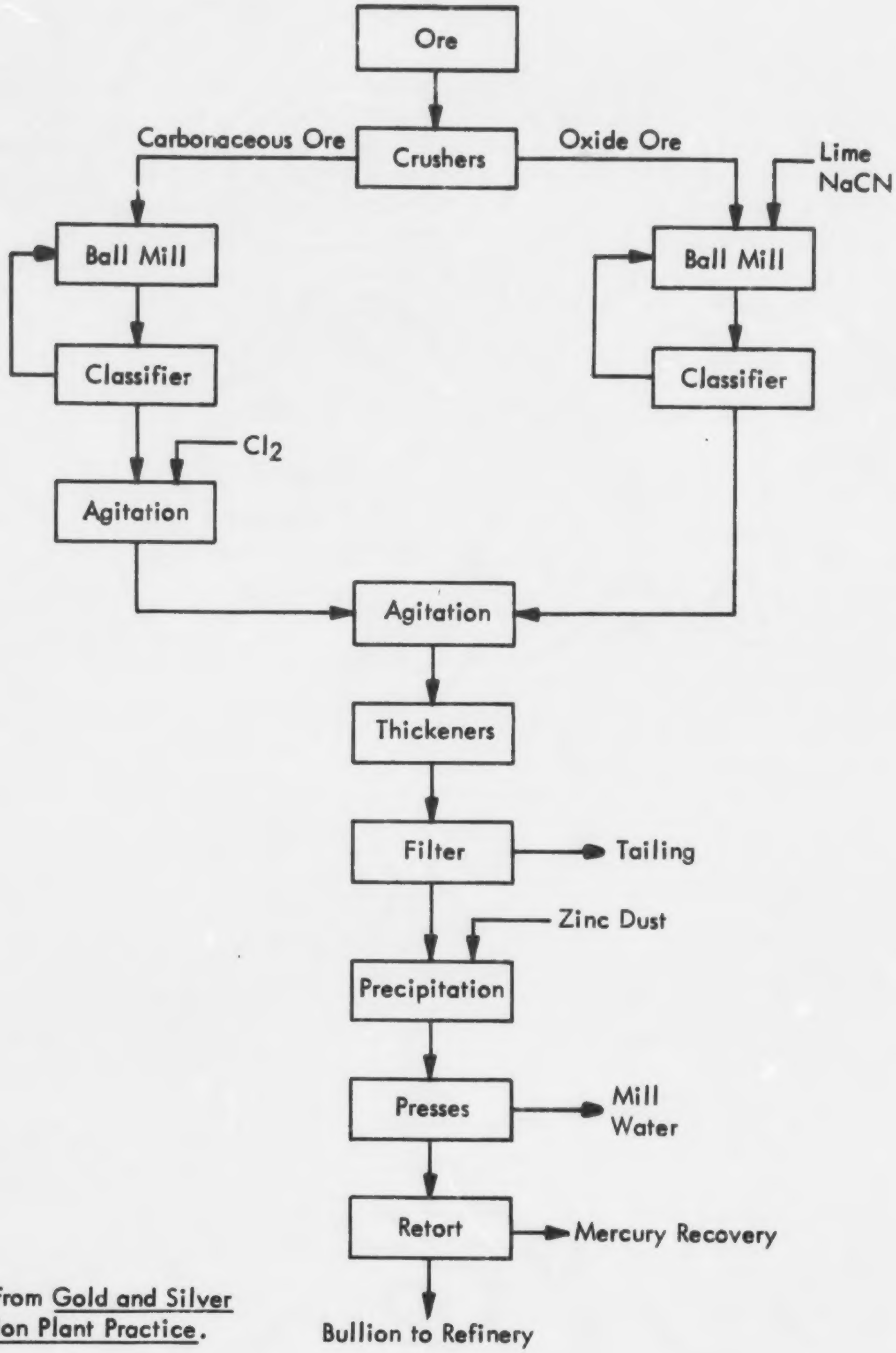
The ore processed at Carlin presents a different set of complications than at Homestake, in that part of the ore is of a carbonaceous origin. Gold ores containing active carbon adsorb gold from the cyanide solution much the same as in a carbon-in-pulp plant, except that the goldloaded carbon cannot be separated from the gangue. Attempts in the past to overcome the deleterious effects of the carbon have included roasting the ore to oxidize the carbon and blanking with kerosene or fuel oil, with varying results.

The Carlin operation (Figure 14) oxidizes the carbonaceous ore with chlorine gas introduced into the pulp. The oxidized, carbonaceous ore then enters the production stream with the oxide ore for agitation dissolution with alkaline cyanide. Gold is recovered as bullion by precipitation with zinc dust and lead acetate. By-product mercury is removed from the gold precipitate by retorting.

Operation at the Cortez mill would appear much the same as the oxide ore portion of the Carlin schematic, Figure 14, except the Cortez mine does not produce by-product mercury. This schematic would apply to ore above 0.08 oz of gold per ton of ore, the mill cutoff grade.[1]

Another part of the process at the Cortez facility is heap leaching of initial development ore and mill cutoff ore less than 0.08 oz/ton. The ore to be leached is piled on an impervious pad, alkaline cyanide solution is sprayed over the heap and the pregnant solution collected in ditches prior to recovery of the gold. The gold is adsorbed onto activated carbon much the same as the Homestake procedure. The carbon is stripped with caustic soda and the gold precipitated onto stainless steel wool cathodes by electrolysis.[1]

It has been reported that Carlin also heap leaches using cyanide solution, but details and the extent of the operation are not available.[4]


Ore
Crushers
Carbonaceous Ore
Oxide Ore
Lime
NaCN
Ball Mill
Classifier
Cl2
Agitation
Ball Mill
Classifier
Agitation
Thickeners
Filter
Tailing
Zinc Dust
Precipitation
Presses
Mill Water
Retort
Mercury Recovery
Bullion to Refinery

Adapted from Gold and Silver Cyanidation Plant Practice.

Figure 14. Carlin process schematic

Knob Hill Mines presents an entirely different operation in that 85% of the gold is recovered by flotation and only the tails (15%) are cyanided. The Knob Hill schematic appears in Figure 15. The gold-silver precipitate from the cyanidization of the flotation tailings is shipped to a smelter along with the flotation concentrates.[1/]

The Magma Copper Company, San Manuel Division, recovers gold by cyanidation of molybdenite concentrates, arising from flotation of copper ore. This process is novel in that most gold in copper sulfide ores follows the copper flotation concentrate and is recovered as a by-product at the smelter.

The Magma process schematic is shown in Figure 16. The process includes vat leaching of the molybdenite concentrates and precipitation of the gold with zinc dust. The molybdenite is further processed to remove water before final shipment.[1/]

Environmental Aspects - Treatment for the destruction of cyanides resulting from cyanidation of gold ores generally entails use of a tailings pond. Tailings ponds can generally be described as reservoirs for retention of water and solids not recovered from the ores.

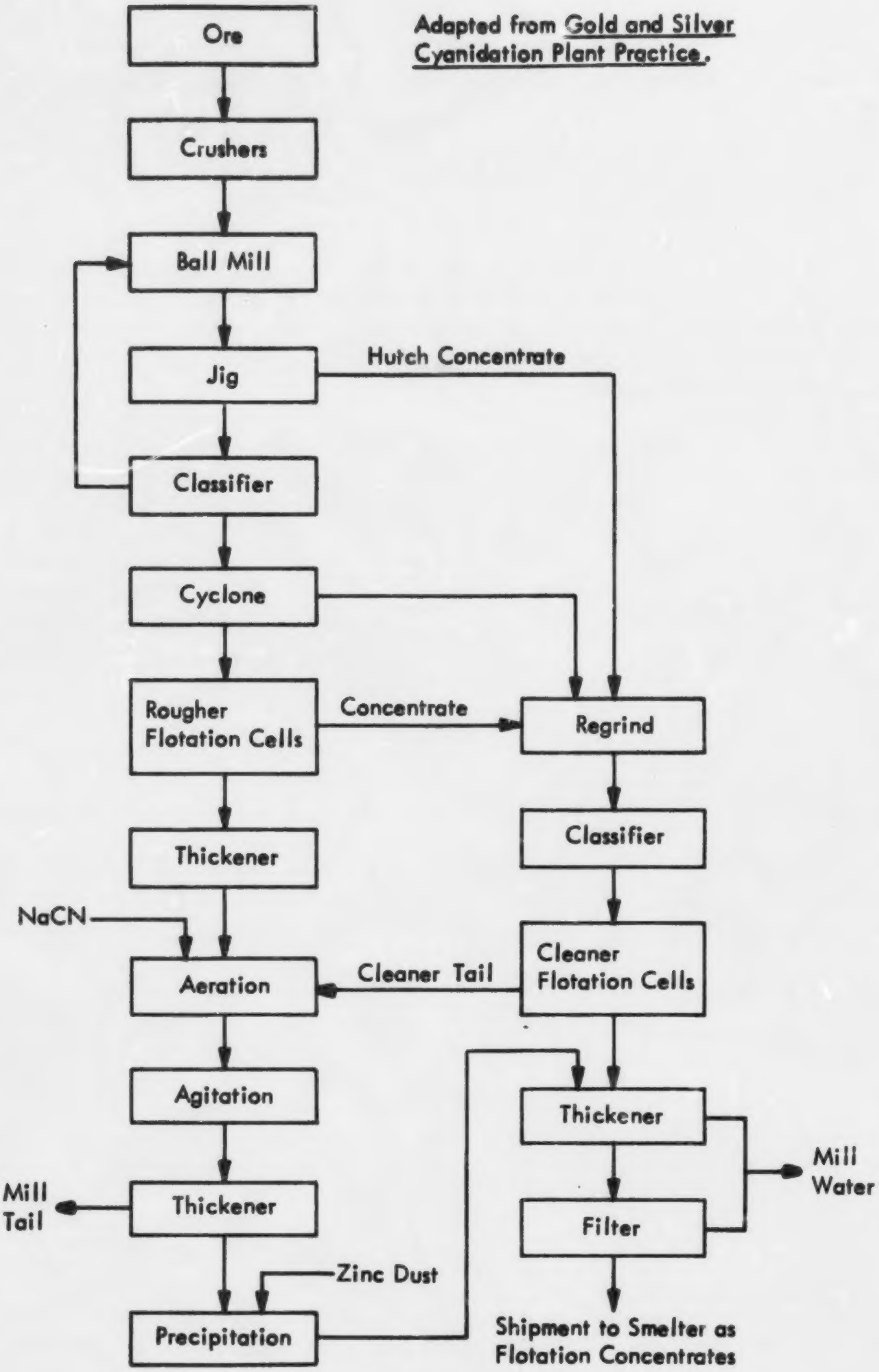
Retention times for tailings ponds vary from a few days to indefinitely depending on various conditions such as: (a) size of pond; (b) water reclaimed; (c) climate; and (d) water runoff from surroundings.

The cyanides may be destroyed in the tailings pond by air oxidation and sunlight. The cyanides may also become immobilized by complexation with metals in solution or by attachment to gangue materials.

Chemical destruction of cyanides at present is not actively practiced. One gold recovery operation has a chlorinator on standby for treatment of tailings pond effluent in case of dam leaks or breaks.[5/]

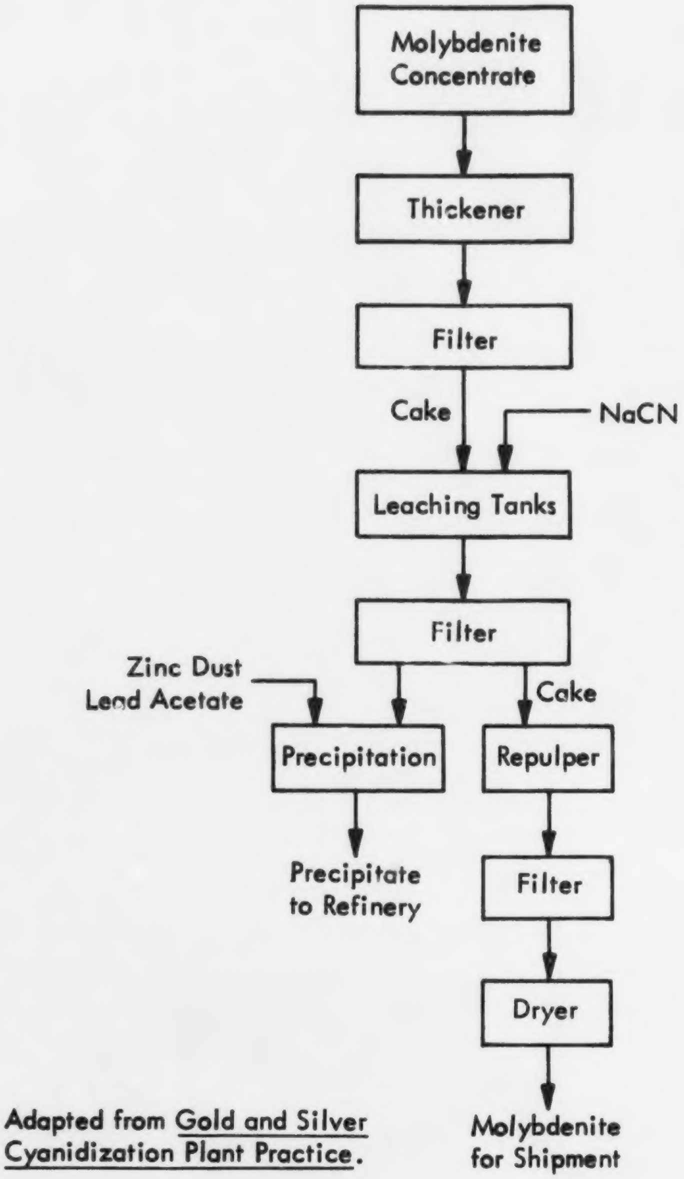
Homestake in the past has discharged the water and tailings from the slime portion of their cyanidation operations to Whitewood Creek.[1/] It has been reported that a treatment process for cyanides is under development.[6/] It is not known if this treatment process has yet been applied to the effluents.

Consumption of Cyanides for Cyanidation - No data are available detailing the actual consumption of cyanides in the gold recovery industries. Figures are available in some cases on consumption of cyanide per ton of ore processed and on the amount of ore processed each year. However, operating conditions affecting the consumption of cyanide per ton of ore processed can change at any given time.


Ore
Crushers
Ball Mill
Jig
Hutch Concentrate
Classifier
Cyclone
Rougher Flotation Cells
Concentrate
Regrind
Classifier
Thickener
NaCN
Aeration
Cleaner Tail
Cleaner Flotation Cells
Agitation
Thickener
Mill Water
Mill Tail
Thickener
Filter
Zinc Dust
Precipitation
Shipment to Smelter as Flotation Concentrates

Adapted from Gold and Silver Cyanidation Plant Practice.

Figure 15. Knob Hill process schematic


Molybdenite Concentrate
Thickener
Filter
Cake
NaCN
Leaching Tanks
Filter
Zinc Dust
Lead Acetate
Cake
Precipitation
Repulper
Precipitate to Refinery
Filter
Dryer
Molybdenite for Shipment

Adapted from Gold and Silver Cyanidization Plant Practice.

Figure 16. Magma process schematic

Conditions changing the consumption of cyanide per ton of ore include: (a) ore grade; (b) cyanicides in the ore; and (c) process changes.

Table 41 details the data for the five major gold cyanidation operations. Figures 17 and 18 detail ore production and total annual cyanide consumption, respectively.

Table 41. CYANIDE CONSUMPTION FOR RECOVERY OF GOLD

Mining operation	Pounds of NaCN per ton of ore	Reference
Homestake Mining Company	Sand portion 0.25 Slime portion 0.75	7 1
Carlin Gold Mining Company	0.28	1
Cortez Gold Mines	(0.25)	
Knob Hill Mines, Inc.	(0.35)	
Magma Copper Company, San Manuel Division	55.3	1

Note: ( ) = MRI estimate.

The projection of future consumption of sodium cyanide for cyanidation of gold and silver ore hinges on several variables. Table 42 lists the variables and the probable effect of each variable.

Selective Flotation

Inorganic cyanides as sodium cyanide, potassium cyanide, calcium cyanide, sodium ferrocyanide, and sodium ferricyanide have been used extensively as chemical additives in froth flotation.

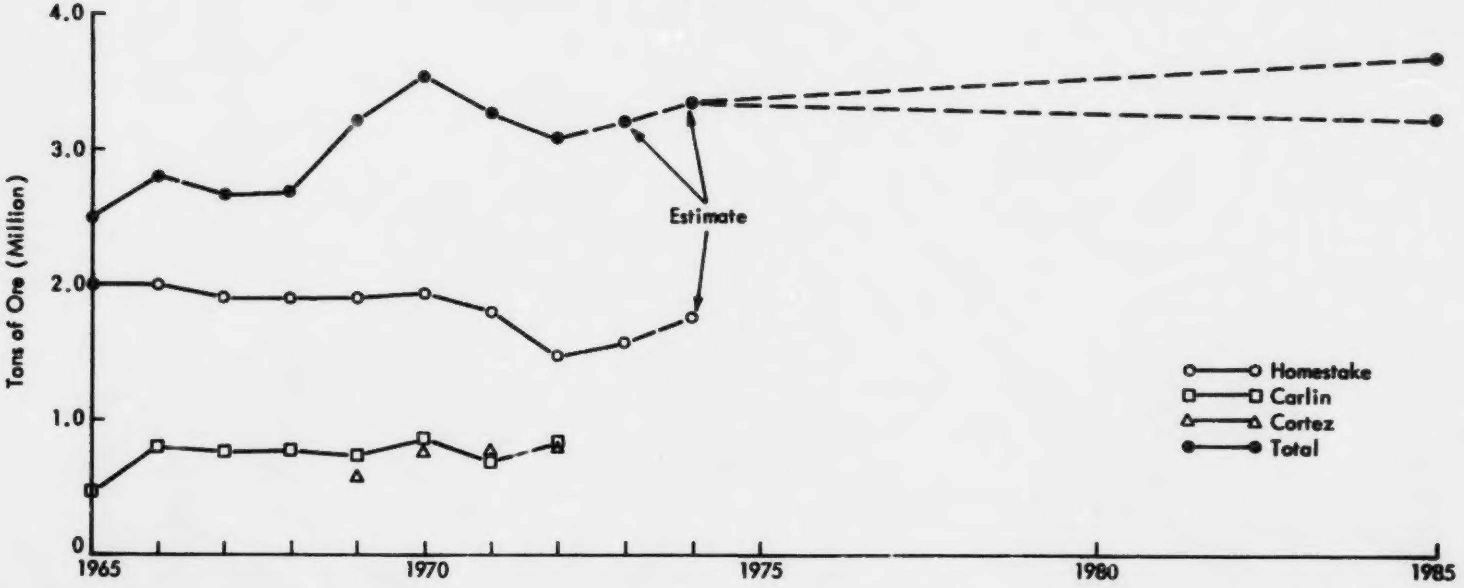


Figure 17. Gold ore production

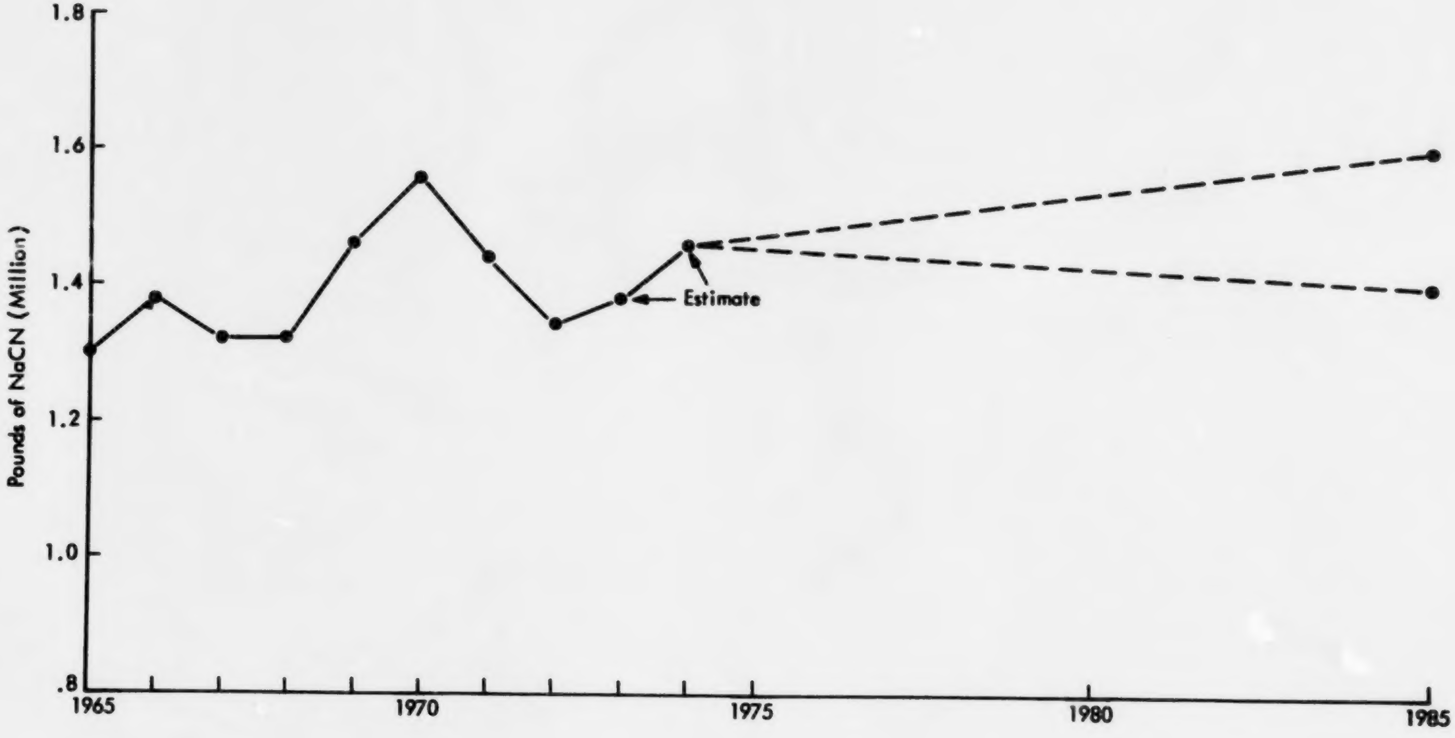


Figure 18. Sodium cyanide consumption for gold recovery by cyanidation

Table 42. FACTORS INFLUENCING CYANIDE CONSUMPTION FOR GOLD RECOVERY

Variable	Effect	Comments
Heap leaching	++	Low capital cost Smaller operations
Price of gold	+	Lowers economical ore grade Extends life of mine Increases bullion production
Availability of developable ore	-	Exploration costs high
Environmental considerations	+	Amalgamation not acceptable
	-	Cyanide destruction costly
Availability of capital	-	

Froth flotation, simply stated, entails separation of mineral values from gangue by the use of (a) a surface active agent; (b) agitation; and (c) air bubbles. The valuable mineral particles are coated with an organic collector; and when a collector-coated particle collides with an air bubble, they will stick together and float to the surface as froth and overflow the flotation cell. Undesirable gangue materials remain in the flotation cell, leaving the bottom of the flotation cell as tailings. Selective froth flotation generally implies the separation of two or more valuable minerals from each other and from the gangue in successive steps.

Froth flotation has been described as being the most important metallurgical process developed in the 20th Century.[8] Froth flotation allows the processing of many millions of tons of ore that otherwise would never have qualified as ore.[9]

Cyanides are used in flotation as depressants to inhibit the attachment of certain minerals to the froth, thereby effecting selective separation. Table 43 shows the general effect of cyanide on various minerals. The use of cyanide in selective flotation has become widespread and indispensable.[10]

Table 43. EFFECT OF CYANIDE ON VARIOUS MINERALS[11,12]

Effect	Mineral name	Chemical composition
Strong depressant	Pyrite	Iron sulfide
	Pyrrhotite	Iron sulfide
	Marcasite	Iron sulfide
	Arsenopyrite	Iron, arsenic sulfide
	Sphalerite	Zinc sulfide
Moderate depressant	Chalcopyrite	Iron, copper sulfide
	Enargite	Copper, arsenic sulfide
	Tennantite	Copper, iron, zinc, silver, arsenic sulfide
	Bornite	Copper iron, sulfide
Not depressant	Galena	Lead sulfide

Ore classifications on which cyanides are used as depressants domestically include:

Copper
Copper-molybdenum
Copper-lead-zinc
Copper-zinc-iron-sulfide
Lead-zinc
Lead-zinc-silver
Zinc
Fluorspar

Other ores on which cyanides are used as depressants, but which are not commonly processed in the U.S. are:

Nickel
Cobalt
Antimony

These ores will not be considered in this report.

The use of cyanide in flotation is generally applied to sulfide minerals, although many oxide ores may be conditioned to respond as the corresponding sulfide mineral.

The most commonly used cyanide as a depressant is sodium cyanide. Calcium cyanide is still in use, but to a much smaller extent than previously, most likely because it is less pure, hence, less easily adapted to automated processes. Sodium ferrocyanide and sodium ferricyanide are used mainly in the flotation separation of copper and molybdenum sulfides. Potassium cyanide is used very little because of higher cost.

Sodium, calcium, sodium ferro- and sodium ferricyanides are usually fed to the flotation circuits as 5% solutions and may be added to the circuit at different points and multiple points depending on the ore treated.[11/]

Usual amounts of the various cyanides fed to the flotation circuit per ton of ore appear below in Table 44.

Table 44. TYPICAL ADDITIONS OF THE CYANIDES TO ORES[11/]

Reagent	Addition (lb/ton)
Sodium cyanide	0.01-0.5
Calcium cyanide	0.01-0.5
Sodium ferrocyanide	0.1-2.0
Sodium ferricyanide	0.1-2.0

Process Descriptions - A generalized description of flotation processes for each ore considered appears in Figure 19.

Ores are difficult to class by type such as copper ore versus copper-molybdenum ore. This will be more evident in Figures 22 and 23 shown later. It should also be noted that when an ore is referred to as a copper-lead-zinc ore, it is actually a copper sulfide ($CuFeS_2$), lead sulfide (PbS), and zinc sulfide (ZnS) ore.

Preparation of the ores for flotation includes size reduction and classification. Minerals vary as to the size most suitable for flotation and ores vary as to the amount of grinding necessary to obtain a substantial degree of mineral liberation. Sulfide minerals can be floated

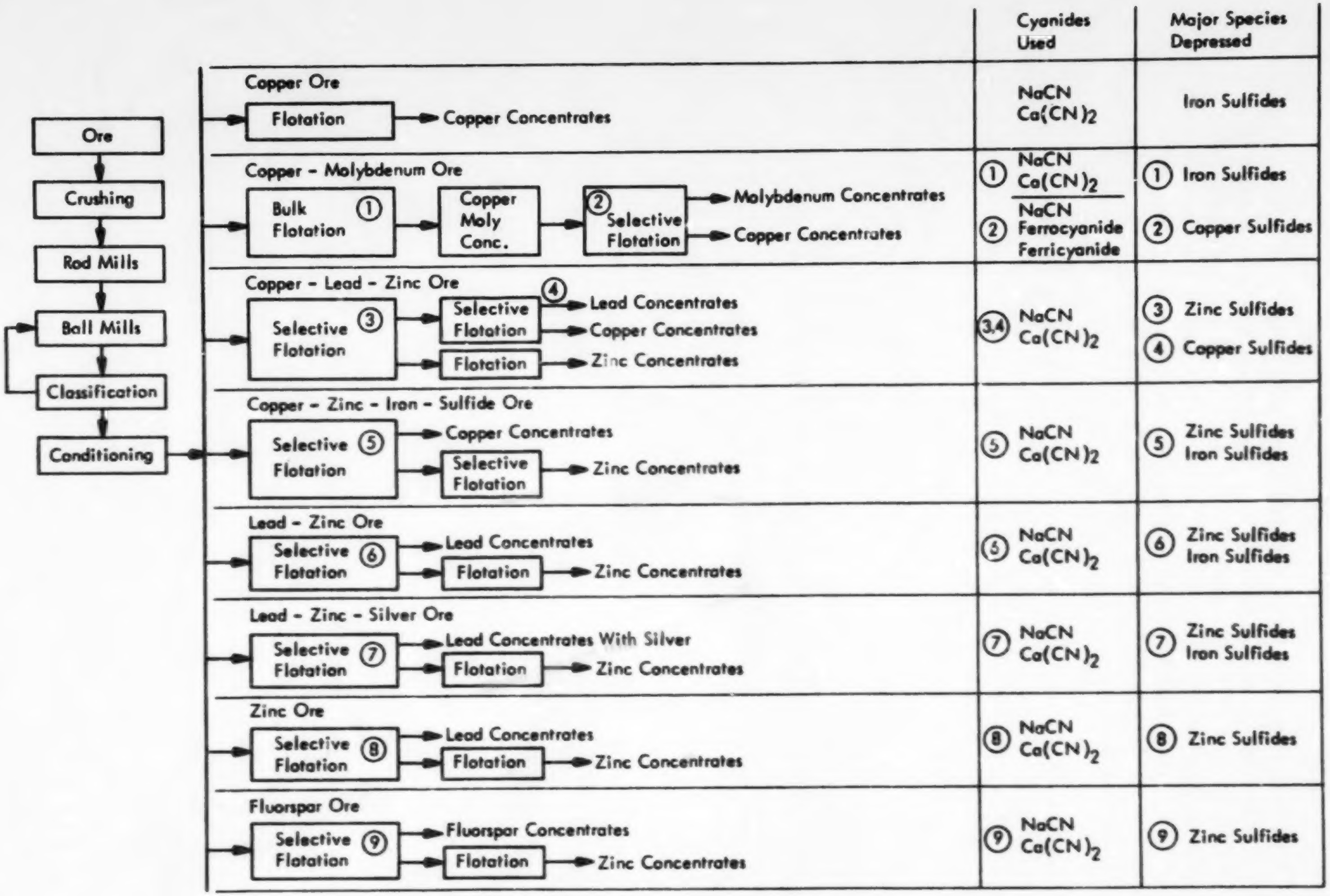

Ore
Crushing
Rod Mills
Ball Mills
Classification
Conditioning
Cyanides Used
Major Species Depressed
Copper Ore
Flotation
Copper Concentrates
NaCN
$Ca(CN)_2$
Iron Sulfides
Copper - Molybdenum Ore
Bulk Flotation ①
Copper Moly Conc.
② Selective Flotation
Molybdenum Concentrates
Copper Concentrates
① NaCN $Ca(CN)_2$
② NaCN Ferrocyanide Ferricyanide
① Iron Sulfides
② Copper Sulfides
Copper - Lead - Zinc Ore
Selective Flotation ③
Selective Flotation ④
Flotation
Lead Concentrates
Copper Concentrates
Zinc Concentrates
3,4 NaCN $Ca(CN)_2$
③ Zinc Sulfides
④ Copper Sulfides
Copper - Zinc - Iron - Sulfide Ore
Selective Flotation ⑤
Copper Concentrates
Selective Flotation
Zinc Concentrates
⑤ NaCN $Ca(CN)_2$
⑤ Zinc Sulfides Iron Sulfides
Lead - Zinc Ore
Selective Flotation ⑥
Lead Concentrates
Flotation
Zinc Concentrates
⑤ NaCN $Ca(CN)_2$
⑥ Zinc Sulfides Iron Sulfides
Lead - Zinc - Silver Ore
Selective Flotation ⑦
Lead Concentrates With Silver
Flotation
Zinc Concentrates
⑦ NaCN $Ca(CN)_2$
⑦ Zinc Sulfides Iron Sulfides
Zinc Ore
Selective Flotation ⑧
Lead Concentrates
Flotation
Zinc Concentrates
⑧ NaCN $Ca(CN)_2$
⑧ Zinc Sulfides
Fluorspar Ore
Selective Flotation ⑨
Fluorspar Concentrates
Flotation
Zinc Concentrates
⑨ NaCN $Ca(CN)_2$
⑨ Zinc Sulfides

Figure 19. Generalized selective flotation process schematic

in the size range of 5 to 420 μ, but flotation should be done at the largest size practicable. Reagent consumption is higher for small particles, and the flotation separation becomes very inefficient for particles less than 5 μ in diameter.

Flotation circuits (Figure 20) generally consist of a bank of roughing cells and a bank of cleaner cells for each mineral recovered. The roughing cells produce a concentrate relatively impure, but containing nearly all of the respective floatable mineral value. The cleaner cells in turn refloat the rougher concentrate, producing a more pure concentrate. The tailings from the cleaner cells are returned to the roughing cells. This dual circuit conserves chemical reagents, produces a higher grade final concentrate and higher percent recovery for each mineral value.

Circled numbers in the following discussion correspond to the numbers in Figure 19 under the respective ore headings.

Copper ore - The vast majority or copper ores are beneficiated by flotation alone or in combination with acid leaching. Sodium and calcium cyanides are used as depressants for iron sulfides commonly associated with copper sulfide deposits. Care must be used when using cyanide as a depressant; when used in excess, it also depresses copper sulfides.[14/]

Lime is used as a pH regulator and also to help depress the iron sulfides, except when gold is present. Sodium carbonate can substitute for the lime to prevent solubilization of gold and silver.

Copper-molybdenum ore - Molybdenum recovery from copper-molybdenum ores would be virtually impossible were it not for flotation, and cyanides are very important in this separation. Sodium and calcium cyanides are used to depress iron sulfides in the initial flotation ① to separate both copper and molybdenum sulfides from the gangue. Then ② sodium cyanide, sodium ferrocyanide and sodium ferricyanide may be used to depress the copper sulfides in the bulk concentrate to produce two concentrates, i.e., molybdenum sulfide from the froth and copper sulfide from the tailing.

Copper-lead-zinc ore - In the flotation of the copper-lead-zinc ores sodium or calcium cyanide may be used to first depress zinc sulfide, sphalerite, while floating a bulk copper-lead concentrate ③ . In this initial step the zinc follows the tails to the zinc flotation circuit. Zinc sulphate is commonly used with cyanide to depress the zinc sulfides. The zinc sulfide is recovered by the addition of copper sulfate which activates the zinc sulfide and renders it floatable.

Adapted from Ref. 13

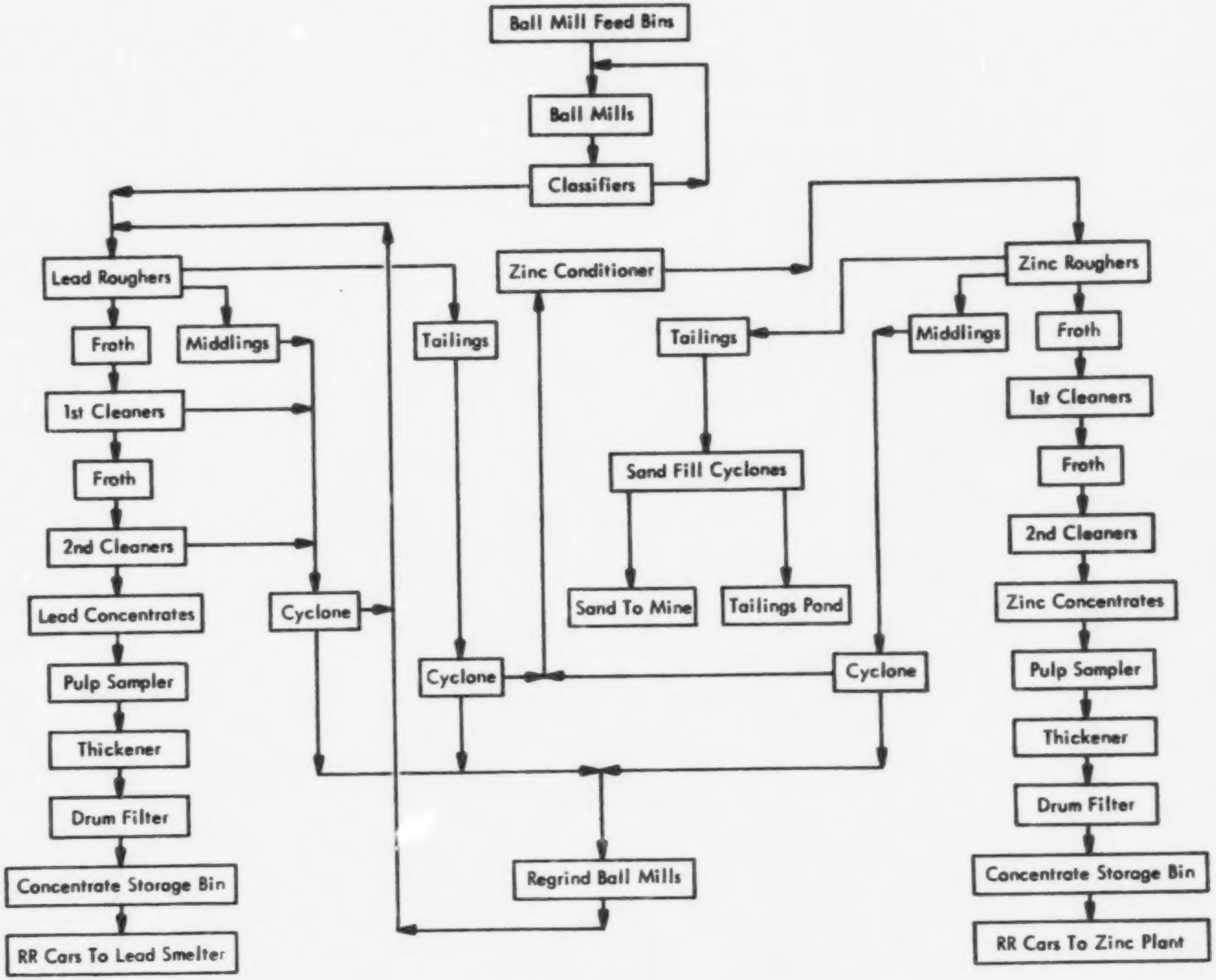

Ball Mill Feed Bins
Ball Mills
Classifiers
Lead Roughers
Froth
Middlings
1st Cleaners
Froth
2nd Cleaners
Lead Concentrates
Pulp Sampler
Thickener
Drum Filter
Concentrate Storage Bin
RR Cars To Lead Smelter
Cyclone
Tailings
Cyclone
Zinc Conditioner
Tailings
Sand Fill Cyclones
Sand To Mine
Tailings Pond
Cyclone
Regrind Ball Mills
Zinc Roughers
Middlings
Froth
1st Cleaners
Froth
2nd Cleaners
Zinc Concentrates
Pulp Sampler
Thickener
Drum Filter
Concentrate Storage Bin
RR Cars To Zinc Plant

Figure 20. Lead-zinc flotation circuits

The bulk copper-lead concentrate in turn is usually selectively floated ④ . The mineral which is less abundant is usually floated away from the more abundant mineral. One method of separation is to depress the copper sulfides with excess sodium or calcium cyanide while floating the lead. The copper remains as a tailing to be further cleaned by flotation to produce a copper concentrate.

Copper-zinc-iron-sulfide ore - In the flotation of copper-zinc-iron-sulfide ores sodium or calcium cyanide may be used to depress the zinc and iron sulfides ⑤ while floating the copper sulfides. In ores of this type copper salts have always coated or activated at least part of the zinc minerals.[13] The cyanide may be helpful by leaching copper from the surface of the zinc minerals, thereby enhancing the depression of the zinc. The cyanide also complexes any stray copper ions in solution. Again care must be used because excess cyanide depresses copper sulfide flotation, and excess copper ions tend to activate the iron sulfides.

The zinc and iron sulfides follow the tailings to the zinc flotation circuit. The separation of the zinc from iron sulfides is usually accomplished best by using sulfide promoters and a pulp pH 8.5 to 11.5.[11] Copper sulfate is used to reactivate the depressed sphalerite. The copper is adsorbed on the surface of the sphalerite particle, which then acts as a copper mineral.

Lead-zinc ore - In the selective flotation of lead-zinc ores ⑥ , sodium and calcium cyanides again are used to depress sphalerite and iron sulfides, much the same as discussed above. Lead-zinc ores often are highly complex, requiring additional grinding to liberate the lead and zinc minerals. Also gold and silver often are present in lead-zinc ores. In these cases the cyanide is usually added in several stages and in small amounts at each stage. In the above cases, recovery efficiency may not be as good as in less complex ores.

Lead-zinc-silver ore - The flotation recovery of lead-zinc-silver ores ⑦ is approximately the same as discussed for lead-zinc ore above. The distinction between the two ores is in the amount of silver present and the economics of recovering the silver. Silver values should be recovered with the lead concentrates to minimize silver dissolution by cyanide and, therefore, the loss of silver.

Zinc ore - The use of sodium and calcium cyanides in the flotation of zinc ore ⑧ is small. The cyanide is used occasionally to depress sphalerite while recovering lead and copper values. Also the cyanide may be used in small quantities to activate the sphalerite by cleaning the sphalerite particle surface prior to activation with copper sulfate.

Fluorspar ore - Sodium and calcium cyanides are used in the flotation of fluorspar (CaF_2) ores ⑨ to depress small amounts of zinc and iron sulfides. This greatly improves the purity of the fluorspar concentrates. In some cases the zinc values may be high enough for recovery, after the removal of the fluorspar values. The recovery of by-product zinc can improve the economics of the fluorspar recovery.

Processing Sites - Table 45 lists in order the 25 leading copper producing mines and corresponding concentrators. In some of the concentrators copper is also recovered by leaching and where possible the capacity for leaching was excluded from the capacity reported.

Table 46 lists in order the 25 leading lead producing mines and corresponding concentrators, if known. These 25 mines produced 99% of the domestic primary lead in 1972. Most of the lead mines situated in Missouri are in the "New Lead Belt" in the southeastern part of the state and account for about 81% of the U.S. production. This area is of recent development since many of these mines began operations in the mid-to-late 1960's.

Table 47 lists companies concentrating fluorspar ores. Some of these companies buy ore and do custom concentration only. Table 47 is not in order of production. The individual company production in most cases has been withheld by the Bureau of Mines to avoid disclosing proprietary data.

Consumption of Cyanides as Depressants - Data on the consumption of the cyanides used as depressants are not complete. The Bureau of Mines has published data outlining the consumption of chemicals used in flotation each 5 years since 1960.[8,21,22/]

Table 48 below details the consumption of cyanides as depressants in the flotation of minerals.

The estimated consumptions in the above Table 48 were made assuming that the consumption of cyanide per ton of ore processed by flotation did not change since 1965.

Table 49 lists various factors affecting the consumption of cyanide per ton of ore.

Table 50 details the consumption (lb/ton) of all depressants including cyanides used in the flotation of the various ores discussed previously.

Table 45. LEADING COPPER PRODUCING MINES 15-17/

1965 Rank	1972 Rank	Mine	County and state	Operator	Products	Capacity (ton/day)	Flotation
1	1	Utah Copper	Salt Lake, Utah	Kennecott Copper Corporation	Cu, Mo, Au, Ag, H_2SO_4, Se, Pd, Pt, Re, Te	108,500	Yes
5	2	San Manuel	Pinal, Arizona	Magma Copper Company	Cu, Mo, Au, Ag	65,000	Yes
2	3	Morenci	Greenlee, Arizona	Phelps Dodge Corporation	Cu, Au, Ag	60,000	Yes
3[a]	4	Berkeley Pit	Silver Bow, Montana	The Anaconda Company	Unknown [b]	Unknown[b]	Unknown[b]
	5	Ray Pit	Pinal, Arizona	Kennecott Copper Corporation	Cu	25,400[c]	Yes
20	6	Pima	Pima, Arizona	Pima Mining Company	Cu, Mo, Au	46,000	Yes
	7	Tyrone	Grant, New Mexico	Phelps Dodge Corporation	Cu, Au, Ag	50,000	
	8	Twin Buttes	Pima, Arizona	The Anaconda Company[d]	Cu	30,000	Yes
	9	Sierrita	Pima, Arizona	Duval Sierrita Corporation	Cu, Mo, Ag	80,000	Yes
9	10	White Pine	Ontonagon, Michigan	White Pine Copper Company	Cu, Ag	25,000	Yes
4	11	Chino	Grant, New Mexico	Kennecott Copper Corporation	Cu, Mo	22,000	Yes
7	12	New Cornelia	Pima, Arizona	Phelps Dodge Corporation	Cu, Au, Ag	34,000	Yes
11	13	Inspiration	Gila, Arizona	Inspiration Consolidated Copper Company	Cu, Mo, Ag, Au, Se, Rh	20,000	Yes
10	14	Mission	Pima, Arizona	American Smelting and Refining Company	Cu, Ag, Mo	22,500	Unknown
6	15	Ruth Pit	White Pine, Nevada	Kennecott Copper Corporation	Cu	21,000	Yes
12	16	Yerington	Lyon, Nevada	The Anaconda Company	Cu	14,000[e]	Yes
8[f]	17	Copper Queen	Cochise, Arizona	Phelps Dodge Corporation	Cu, Au, Ag	20,000	Yes
19	18	Mineral Park	Mohave, Arizona	Duval Corporation	Cu, Mo, Ag	17,000	Unknown
17	19	Copper Cities	Gila, Arizona	Cities Service Company	Cu	14,000[e,g]	Yes[g]
15	20	Silver Bell	Pima, Arizona	American Smelting and Refining Company	Cu, Mo, Ag	11,000	Yes
3[a]	21	Butte Hill	Silver Bow, Montana	The Anaconda Company	Cu, H_2SO_4, Ag, Au, Se	50,000	Yes
8[f]	22	Lavender Pit	Cochise, Arizona	Phelps Dodge Corporation	Cu, Au, Ag	[h]	[h]
16	23	Bagdad	Yavapai, Arizona	Bagdad Copper Corporation	Unknown	Unknown	Yes
18	24	Magma	Pinal, Arizona	Magma Copper Corporation	Cu	3,500[i]	Yes[i]
	25	Copper Canyon	Lander, Nevada	Duval Corporation	Cu, Au, Ag[j]	4,000[j]	Yes[j]

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[a] Berkeley Pit and Butte Hill mines combined
[b] May be included with Butte Hill mine data.
[c] Excludes acid leaching plant.
[d] Now a joint venture with American Metal Climax Company called Anamax Mining Company.
[e] Includes acid leaching plant.
[f] Copper Queen and Lavendar Pit combined.
[g] Miami Copper Operations, Gila, Arizona.
[h] May be included with Copper Queen data.
[i] Superior Division, Pinal, Arizona.
[j] Battle Mountain Properties, Lander Nevada.

Table 46. LEADING LEAD PRODUCING MINES[16,18,19]

1965 Rank	1972 Rank	Mine	County and state	Operating company	Products	Capacity (ton/day)	Flotation	Comments
	1	Buick	Iron, Missouri	AMAX Lead Company of Missouri	Pb, Zn, H_2SO_4	5,000	Yes	
	2	Fletcher	Reynolds, Missouri	St. Joe Minerals Corporation	Pb, Zn, Cu	5,000	Yes	Mill started 2/67
	3	Magmont	Iron, Missouri	Cominco American, Inc.	Pb, Zn, Cu, Ag	4,200	Yes	Mill started 6/68
	4	Ozark	Reynolds, Missouri	Ozark Lead Company	Pb, Zn	6,000	Yes	
1a/	5	Viburnum No. 29	Washington, Missouri	St. Joe Minerals Corporation	Pb, Zn, Cu	7,000	Yes	
2	6	Federal	St. Francois, Missouri	St. Joe Minerals Corporation	Unknown	Unknown	Unknown	Closed 1972
1a/	7	Viburnum No. 28	Iron, Missouri	St. Joe Minerals Corporation	a/	a/	a/	
3	8	Bunker Hill	Shoshone, Idaho	The Bunker Hill Company	Pb, Zn, Ag	2,400	Yes	
5	9	Lucky Friday	Shoshone, Idaho	Hecla Mining Company	Pb, Cu, Zn, Au, Ag Cd	800	Yes	
17	10	Burgin	Utah, Utah	Kennecott Copper Corporation	Pb, Zn, Ag, Cdb/	500b/	Yesb/	
1a/	11	Viburnum No. 27	Crawford, Missouri	St. Joe Minerals Corporation	a/	a/	a/	
7	12	Star Morning	Shoshone, Idaho	Hecla Mining Company	Zn, Pb, Ag	1,000	Yes	
6c/	13	Indian Creek No. 32	Washington, Missouri	St. Joe Minerals Corporation	Pb, Zn	2,200	Yes	
8	14	Idarado	Ouray and San Miguel, Colorado	Idarado Mining Company	Zn, Pb, Cu, Au, Ag, Cd	1,700	Yes	
	15	Leadville	Lake, Colorado	American Smelting and Refining Company	Pb, Zn, Ag	700	Yes	
	16	Dayrock	Shoshone, Idaho	Day Mines, Inc.	Pb, Ag, Zn, Cu, Au	240	Yes	
6c/	17	Indian Creek	Washington, Missouri	St. Joe Minerals Corporation	c/	c/	c/	
16	18	Sunnyside	San Juan, Colorado	Standard Metals Corporation	Zn, Pb, Ag, Cd, Au	700	Yes	
	19	Camp Bird	Ouray, Colorado	Federal Resources Corporation	Pb, Zn	500	Unknown	
24	20	Ground Hog	Grant, New Mexico	American Smelting and Refining Company	Zn, Pb, Cu, Ag	450	Unknown	
12	21	Mayflower	Wasatch, Utah	Hecla Mining Company	Unknown	Unknown	Unknown	
15	22	Austinville Ivanhoe	Wythe, Virginia	New Jersey Zinc Company	Zn, Pb	2,600	Yes	
18	23	Eagle	Eagle, Colorado	New Jersey Zinc Company	Zn, Pb, Cu, Agd/	1,200d/	Yesd/	
14	24	Pend Oreille	Pend Oreille, Washington	Pend Oreille Mines and Metals Company	Pb, Zn	2,400	Yes	
	25	Bulldog Mountain	Mineral, Colorado	Homestake Mining Company	Pb, Ag	300	Yes	
	e/	Brushy Creek	Reynolds, Missouri	St. Joe Minerals Corporation	Pb, Zn	5,000	Yes	Mill started 6/73

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a/ Viburnum No. 28 and No. 27 included with Viburnum No. 29.
b/ Tintic Division, Utah, Utah.
c/ Indian Creek No. 23 included with Indian Creek No. 32.
d/ Gilman Mine, Eagle, Colorado.
e/ 1974 production would place Brushy Creek in top 10 mines.

Table 47. COMPANIES CONCENTRATING FLUORSPAR[16,20]

Company	Concentration location county and state	Products (in addition to fluorspar)	Capacity (ton/day)	Flotation
Ozark-Mahoning Company	Hardin, Illinois	Zn, Pb	576	Yes
	Jackson, Colorado	None	600	Unknown
Minerva Oil Company, Fluorspar Division	Hardin, Illinois	Zn, Pb, $BaSO_4$	434	Yes
	Hardin, Illinois	None	250	Yes
Cerro Spar Corporation	Livingston, Kentucky	Zn, Pb	Unknown[a]	Unknown[a]
Roberts Mining Company	Ravalli, Montana	None	1,200	Unknown
E. G. Sommerlath Enterprises	Crittenden, Kentucky	Barite, Zn Pb, silica	250	No
Win Industries, Inc.	Cochise, Sierra New Mexico	None	150	Yes
Bullion Monarch Company	Lander, Nevada	Sb, Ag, Au, Pb, Zn, W	800	Yes
Reynolds Metals Company	Maverick, Texas	None	500	Unknown

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a/ Concentrator to open in 1974.

Table 48. CONSUMPTION OF CYANIDES AS FLOTATION REAGENTS IN POUNDS

	1960[8]	1965[21]	1970[22]
Calcium cyanide	806,285	85,509	(small)
Sodium cyanide	2,805,900	3,224,208	(4,000,000)
Potassium cyanide	(small)	(small)	(small)
Sodium ferrocyanide	514,467	941,053	(1,500,000)
Sodium ferricyanide	(small)	(small)	(small)

( ) = MRI estimate.

Table 49. FACTORS AFFECTING CYANIDE CONSUMPTION

Factor	Effect	Comments
Automated process control	-	Resulted in discontinued use at Friedensville Mine[23]
Change from calcium to sodium cyanide	-	
Environmental considerations	-	
New, more specific depressants	-	
Lower grade ores	+	
Smelter specifications	+	

Table 50. CONSUMPTION OF ALL DEPRESSANTS (INCLUDING CYANIDES) PER TON OF ORE[8,21,22]

Ore type	Total depressant consumption (lb/ton) 1960	1965	1970
Copper	0.008	0.004	0.006
Copper-molybdenum	0.048	0.065	0.054
Copper-lead-zinc	0.801	0.444	0.626
Copper-zinc-iron-sulfur	0.222	0.163	0.191
Lead-zinc	0.060	0.037	0.269
Lead-zinc-silver	-	0.502	0.564
Zinc	-	0.034	0.070
Fluorspar	2.790	2.275	2.695

Figure 21 shows graphically the consumption (millions of pounds as NaCN) of cyanides used as depressants in the flotation of minerals, and also the projected consumption (as NaCN) of cyanides through 1985.

Figures 22, 23, and 24 depict the total production of copper, lead-zinc and fluorspar bearing ores as well as the beneficiation of the respective ores by flotation. The apparently greater tonnage of ore beneficiated than produced most likely results from the overlap of the types of ores. Copper-lead-zinc and copper-zinc-iron-sulfide ores would likely appear not only in copper bearing ores beneficated by flotation, Figure 22, but also in lead-zinc bearing ores beneficated by flotation, Figure 23.

Environmental Considerations - Disposal of flotation solutions containing cyanides generally entails the use of tailings ponds, much the same as discussed in the preceding section on cyanidation of gold and silver ores (p. 93).

No active chemical destruction of cyanides is generally practiced in the flotation recovery of minerals and metals. Alkaline chlorination, ozonation or other chemical oxidation of cyanides could be applied technically to the flotation industry; however, in nearly all instances the costs would be prohibitive because of the extremely large gallonage of water consumed. Of consideration also is the generally low consumption of cyanides per ton of ore processed by flotation and the usual practice of recycling water to the mill where possible.

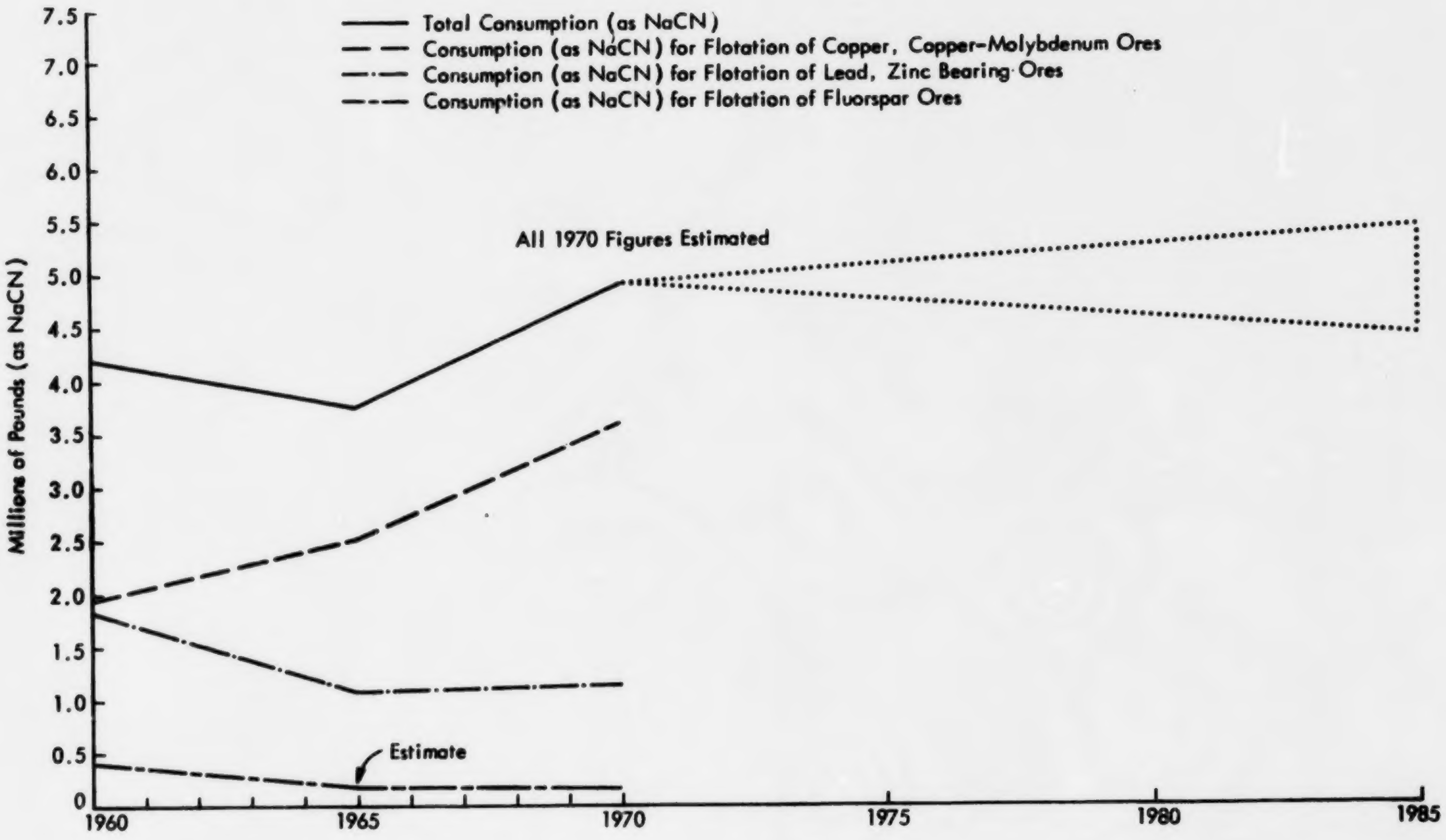

Figure 21. Cyanide consumption as a flotation reagent (as NaCN)

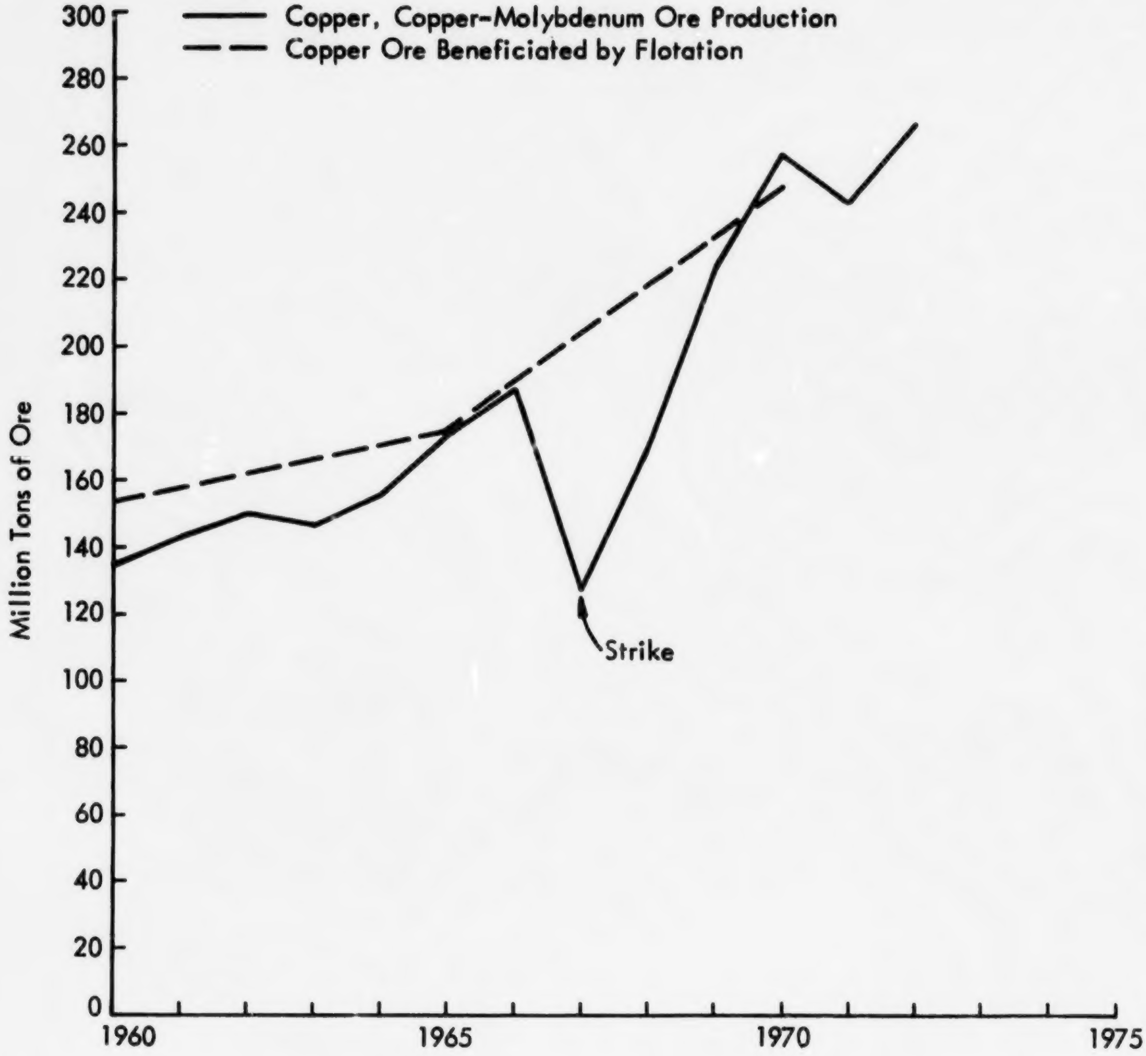

Figure 22. Copper bearing ore production and beneficiation by flotation

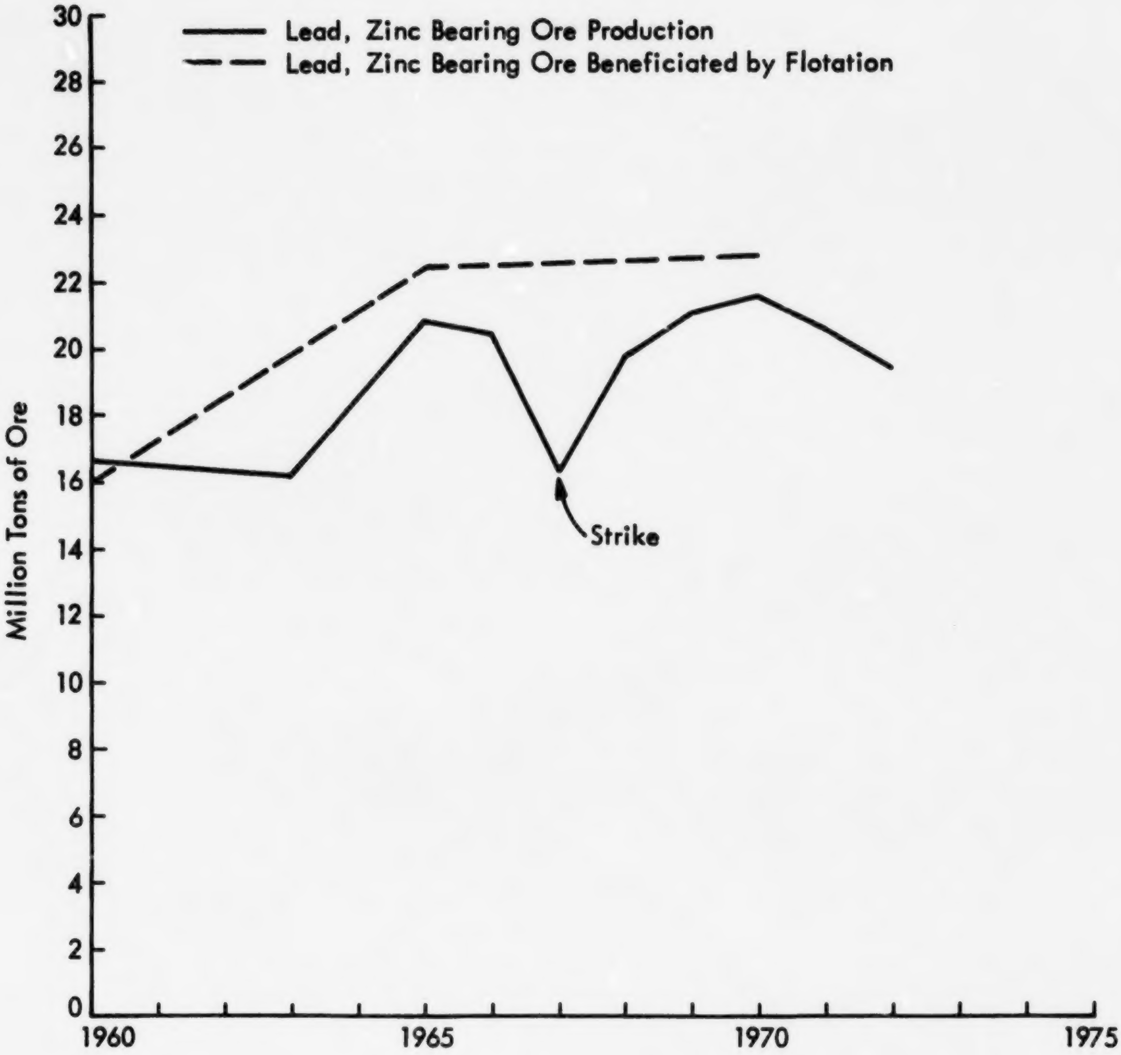

Figure 23. Lead-zinc bearing ore production and beneficiation by flotation

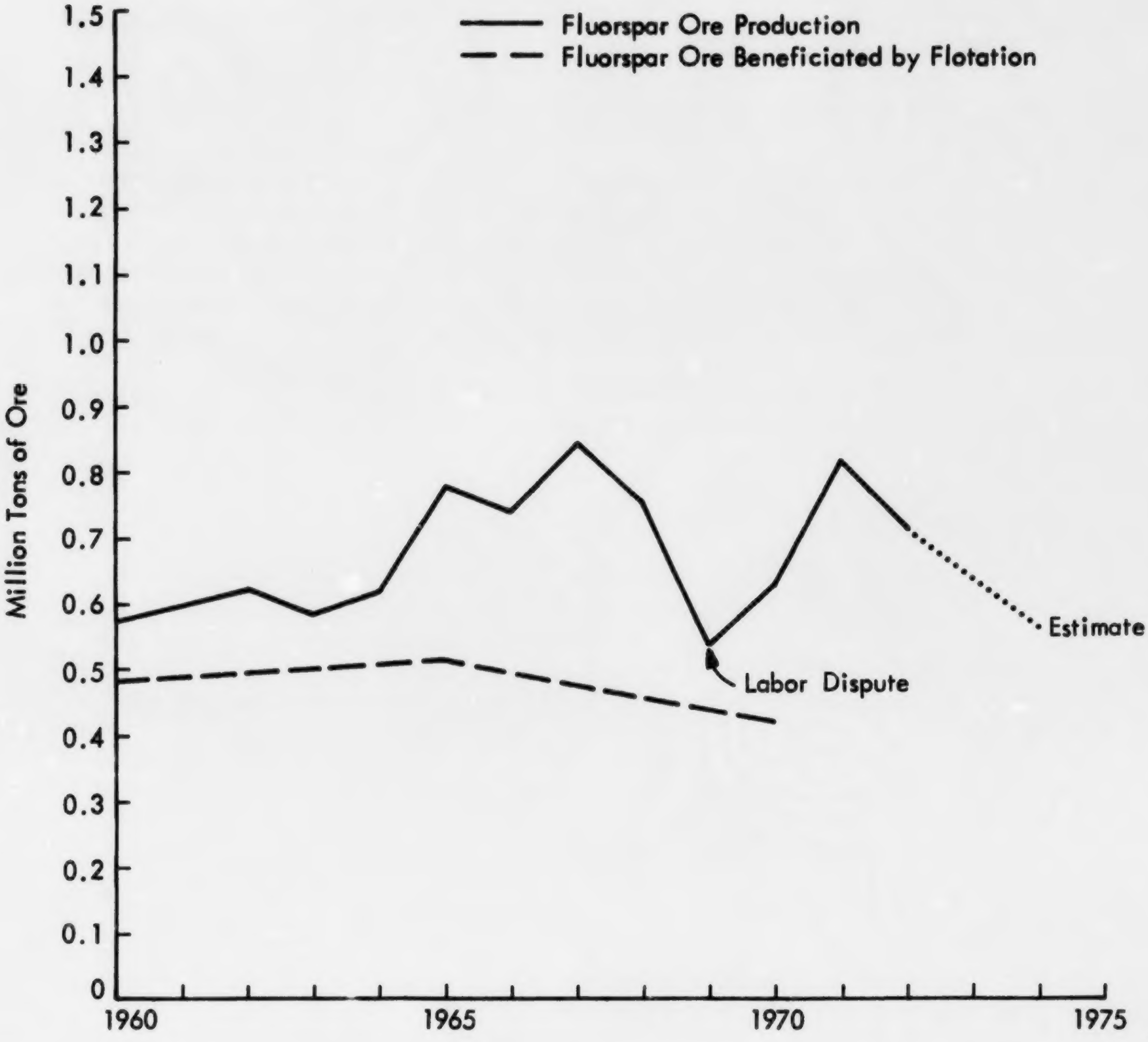

Figure 24. Fluorspar ore production and beneficiation by flotation

Most of the cyanide is adsorbed strongly on the surfaces of the minerals in the tailings pond, and is not found in the water in the tailings pond.

The proper use of tailings ponds seems the only feasible method of cyanide destruction.

METAL HEAT TREATMENT (5.6%)

Sodium cyanide and occasionally potassium cyanide, calcium cyanide and sodium ferrocyanide are used in metal heat treating to produce case hardness. The processes for case hardening of metals using cyanides are: (a) liquid carburizing; (b) liquid nitriding; (c) liquid carbonitriding. These processes vary mainly in salt bath composition and temperature as will be discussed under separate subsections.

Case hardening is a process for treating metals producing a hard, wear-resistant, relatively thin surface (case) leaving the interior (core) strong and tough.[1]

Process Descriptions

Liquid Carburizing.[2] - Case hardening by carburizing adds carbon to the surface of steel.[2] The nature of the source of carbon distinguishes between gas, liquid, or pack carburizing. Gas carburizing, using carbon monoxide or methane, is the most prevalent, and pack carburizing, using coke, the least used. Liquid carburizing uses cyanide as the source of carbon.

Liquid carburizing is accomplished by submerging the part to be case hardened in a molten salt bath containing sodium cyanide. The immersion time and the temperature of the bath depend on depth of the case desired. The pot containing the salt bath may be externally heated with oil or gas or internally heated with immersed electrodes. After holding the part in the salt bath for the period of time required, the part is quenched in water, brine or oil, depending on final properties desired.

Typical bath compositions for liquid carburizing are shown below in Tables 51 and 52. Bath compositions vary depending on the desired depth (thickness) of the case and the operating temperature of the bath.

Table 51. COMPOSITIONS OF LIQUID CARBURIZING SALT BATHS[3]

Compound	% Composition Light case	Deep case
Sodium cyanide	10-23	6-16
Barium chloride	0-40	30-55
Calcium or strontium chloride	0-10	0-10
Potassium chloride	0-25	0-20
Sodium chloride	20-40	0-20
Sodium carbonate	30 max	30 max
Accelerators[a]	0-5	0-2
Sodium cyanate	1.0 max	0.5 max

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[a] Possible accelerators include: manganese dioxide, boron oxide, sodium fluoride, silicon carbide.

Table 52. PREFERRED NaCN CONTENT IN RELATION TO THE BATH TEMPERATURE[3]

Bath temperature (°F)	NaCN Content (%) Min.	Preferred	Max.
1500	14	18	23
1550	12	16	20
1600	11	14	18
1650	10	12	16
1700	8	10	14
1750	6	8	12

The salt baths are usually operated using a carbon or graphite cover floating on the salt bath to retard oxidation of the cyanide.

Bath temperature is adjusted for the case depth desired. A temperature range of 1550 to 1650°F generally is used to produce a case depth in the range 0.003 to 0.030 in. The range 1650 to 1750°F is used to develop case depths of 0.020 to 0.120 in. Higher temperatures can be used, but the life of the salt bath and the equipment is shortened. Carbon penetration is more rapid at elevated temperatures, which may be advantageous to production.[3]

Liquid carburizing produces a case containing mostly carbon throughout the case, and some nitrogen on the exterior portion of the case.[3/]

Reactions taking place in the bath include the following:[3/]

1. $2\ NaCN \longrightarrow Na_2CN_2 + C$
2. $2\ NaCN + O_2 \longrightarrow 2\ NaOCN$
3. $NaCN + CO_2 \longrightarrow NaOCN + CO$
4. $NaOCN + C \longrightarrow NaCN + CO$
5. $4\ NaOCN + 2O_2 \longrightarrow 2\ Na_2CO_3 + 2CO + 4N$
6. $4\ NaOCN + 4CO_2 \longrightarrow 2\ Na_2CO_3 + 6CO + 4N$

and in high temperature baths

7. $Ba(CN)_2 \longrightarrow BaCN_2 + C$

The case is formed on the part by the following reactions:[3/]

8. $3Fe + 2CO \longrightarrow Fe_3C + CO_2$
9. $3Fe + C \longrightarrow Fe_3C$

Liquid Nitriding - Liquid nitriding is a process for case hardening of steel by the addition of nitrogen to the surface. Liquid nitriding produces an extremely hard, wear-resistant surface, resisting softening by temperature and corrosion.[4/]

The major differences in practice between liquid carburizing and liquid nitriding are (a) bath temperature, and (b) bath compositions. Liquid nitriding salt bath operating temperatures are normally between 950 to 1050°F.[4/]

Table 53 lists three liquid nitriding salt bath compositions.

Case depth in liquid nitriding varies with the different steels nitrided, but generally is less than 0.020 in. and often in the range 0.002 to 0.005 in.

Table 53. DIFFERENT LIQUID NITRIDING SALT BATH COMPOSITIONS[5]

Compound	Composition (%) 1	2	3
Sodium cyanide	30.00 max.	58-68	60-61
Sodium carbonate	25.00[a] max.	1.5-1.8	
Sodium cyanate		0.3-0.35	
Potassium cyanide		29-38	
Potassium carbonate	a/	0.2	15-15.5
Potassium cyanate		0.2-0.3	
Potassium chloride	remainder	0.2	23-24
Other active ingredients	4.00 max.		

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[a] Potassium carbonate may be substituted for sodium carbonate.

Equipment used for liquid nitriding can be the same as that used for liquid carburizing.

The nascent nitrogen at the metal surface necessary for nitriding is produced by the cyanate which results from the oxidation of cyanide (see the reactions Nos. 5 and 6, p. 118). For this reason, liquid nitriding salt baths must be aged prior to introduction of metal to be nitrided. In aging, the salt bath is held at 1050 to 1100°F for at least 12 hr.[5] The liquid nitriding salt bath, unlike the liquid carburizing salt bath, is operated without a floating graphite cover.

Liquid Carbonitriding - Liquid carbonitriding is a process for production of a file hard, wear-resistant surface on ferrous parts.[6] Liquid carbonitriding is commonly referred to as cyaniding.

Liquid carbonitriding is essentially a combination of liquid carburizing and liquid nitriding. The hardened case is produced by nitrogen and carbon both reacting with the iron near the surface.

A preferred bath composition for liquid carbonitriding appears in Table 54.

Table 54. PREFERRED SALT BATH COMPOSITION FOR LIQUID CARBONITRIDING[4]

Compound	Composition (%)
Sodium cyanide	30
Sodium carbonate	40
Sodium chloride	30

Case depths are usually on the order of 0.010 in. thick. Bath operating temperatures vary usually between 1400 and 1600° F.[6] Salt bath equipment is the same as employed for liquid carburizing or liquid nitriding. The salt baths are generally operated without a graphite covering material, but if a cover is used, oxygen or carbon dioxide must be bubbled through the salt bath to oxidize the cyanide.

Below are reactions taking place in the bath producing nascent carbon and nitrogen necessary for the case hardening by liquid carbonitriding:[6]

$$2NaCN + O_2 \longrightarrow 2NaOCN$$

$$4NaOCN \longrightarrow Na_2CO_3 + 2NaCN + CO + 2N$$

$$2CO \longrightarrow CO_2 + C$$

$$NaCN + CO_2 \longrightarrow NaOCN + CO$$

Another much less used method for carbonitriding in selective case hardening is to heat the part to red heat, sprinkle on a cyanide salt and reheat in a forge or lead bath. Sodium cyanide or sodium ferrocyanide may be used in this application. Sodium ferrocyanide is preferred due to its less toxic nature.[6]

Processing Sites

The number of commercial and captive heat treaters is large. Commercial heat treaters may be thought of as a "jobber" doing business with one or more outside customers on the open market. Captive heat treaters may be described as being owned and operated by the company for which the work is being done. Table 55 summarizes the various estimates of numbers for the different categories of heat treaters. The distribution of heat treating shops is closely aligned with industrial activity.

Table 55. ESTIMATES OF THE NUMBER OF COMMERCIAL
AND CAPTIVE HEAT TREATING SHOPS

Type	Number	Reference	Comments
Commercial	938	7	in 1972
Captive	9,000-10,000	7	in 1972
Commercial	600	8	≥ 20 employees
Captive	9,500	8	

It should be pointed out that the majority of the above commercial and captive heat treaters do not use cyanide salt baths for heat treating. An estimated 2,500 commercial and captive heat treaters may use cyanide salt baths for liquid carburizing, liquid nitriding and liquid carbonitriding.[9]

Due to the capital investment required to dispose of cyanide wastes, only the larger commercial heat treaters offer heat treating processes utilizing cyanide salt baths. Captive shops may differ somewhat, due to the backing received from the parent company. Also, captive shops may tend toward more specific requirements, some of which may include use of cyanide salt baths.

Environmental Management

Cyanide wastes or losses in metal heat treating processes arise generally from two sources: (a) quenching and (b) pot cleanout. By far the most important of these is the losses incurred during quenching.

The processes for case hardening by liquid carburizing, liquid nitriding and liquid carbonitriding all include: (a) submerging the parts in the cyanide salt bath; (b) maintaining the salt bath at the required temperature; (c) holding the parts submerged for the required time; (d) withdrawing the parts while hot; and (e) quenching the parts. When the parts are withdrawn from the bath, liquid salt adheres to the surface of the parts. This salt is removed when the parts are quenched.

The quenching medium may be water, water containing dissolved salts, or oil. In the event an aqueous quenching medium is used, the salt adhering to the parts is dissolved in the quenching solution. If oil is used for the quench, then the adhering salt is not soluble and settles to the bottom of the quenching tank as a sludge.

A less significant source of cyanide wastes results from cleaning out the pot containing the salt bath. The pot may need to be cleaned out for replacement of the salt because of sludge buildup or for replacement of the pot due to the corrosive and erosive action of the salt and heat.

Disposal of cyanide wastes produced by heat treating is predominantly accomplished by oxidation of an alkaline solution containing the cyanide with chlorine gas, sodium hypochlorite or calcium hypochlorite. In the cases where oil quench sludges or concentrated salts from pot cleanout must be disposed of, the cyanide wastes must be dissolved in water prior to treatment.

Less used waste treatment systems include: (a) electrolytic destruction;[10] (b) peroxide-formaldehyde oxidation (Kastone process);[10] (c) ozonation; (d) solid waste disposal in landfills; and (e) concentration and recovery.[11]

In many cases, a combination of electrolytic and alkaline-chlorination may offer an economic advantage; for instance, initial treatment of concentrated cyanide wastes by electrolysis to a low level of cyanide concentration, followed by chlorination to reduce the cyanide to less than 1 ppm concentration.

Another consideration in the waste treatment of heat treating wastes is that complex iron cyanides will likely be formed from the reaction of cyanide with the ferrous salts. Iron cyanides do not respond well to conventional alkaline chlorination. The alkaline chlorination may need to be supplemented with heat.

The disposal of solid wastes to landfills could be potentially hazardous due to the solubility of many cyanide salts used in metal heat treating. The disposal of solid cyanide wastes in landfills may lead to leaching of the cyanides and eventual contamination of water courses.

Cyanide Consumption

Currently there are five major companies supplying salt baths containing cyanide for metal heat treating, as follows:

1. Heatbath Corporation, Springfield, Massachusetts
2. E. F. Houghton and Company, Norristown, Pennsylvania
3. Kolene Corporation, Detroit, Michigan

4. The Mitchell-Bradford Chemical Company, Milford, Connecticut

5. Park Chemical Company, Detroit, Michigan

No definitive data have been collected on the usage of cyanides for metal heat treating. MRI based the consumption of sodium cyanide for metal heat treating, Figure 25, on estimates from the four companies above, except the Mitchell-Bradford Chemical Company, which did not estimate annual consumption.

Estimates were based on individual company data and knowledge of their relative position in sales. Estimates ranged from 3 to 7 million pounds of sodium cyanide consumed annually, with the average 4 to 5 million pounds.

Figure 25 shows a general decline in the consumption of sodium cyanide over the past 10 years. The projection to 1985 also anticipates a continued decline in consumption.

Table 56 includes some of the factors most likely to influence future consumption.

In summary, even though cyanide salt baths have advantages over alternatives, the future consumption will likely decrease.

PHOTOGRAPHIC PROCESSING (3.1%)

Potassium and sodium ferro- and ferricyanides are used in photographic processing as a silver bleach for color motion pictures, color TV film, and in color photofinishing. Other uses of these cyanides are for image reduction (i.e., density reduction) and silver recovery from black-and-white film. However, the latter two uses represent very small and limited application areas.

All major modern color processes utilize a silver halide emulsion as the light sensitive portion of the film. The latent image is developed to a black silver image and a color dye image formed coincidently through use of a color developing agent. Some color couplers are contained in the emulsion while others, as with certain color reversal films, are introduced by the developing solutions. The color developing agents and details of the emulsion are proprietary and lie outside the scope of this report.

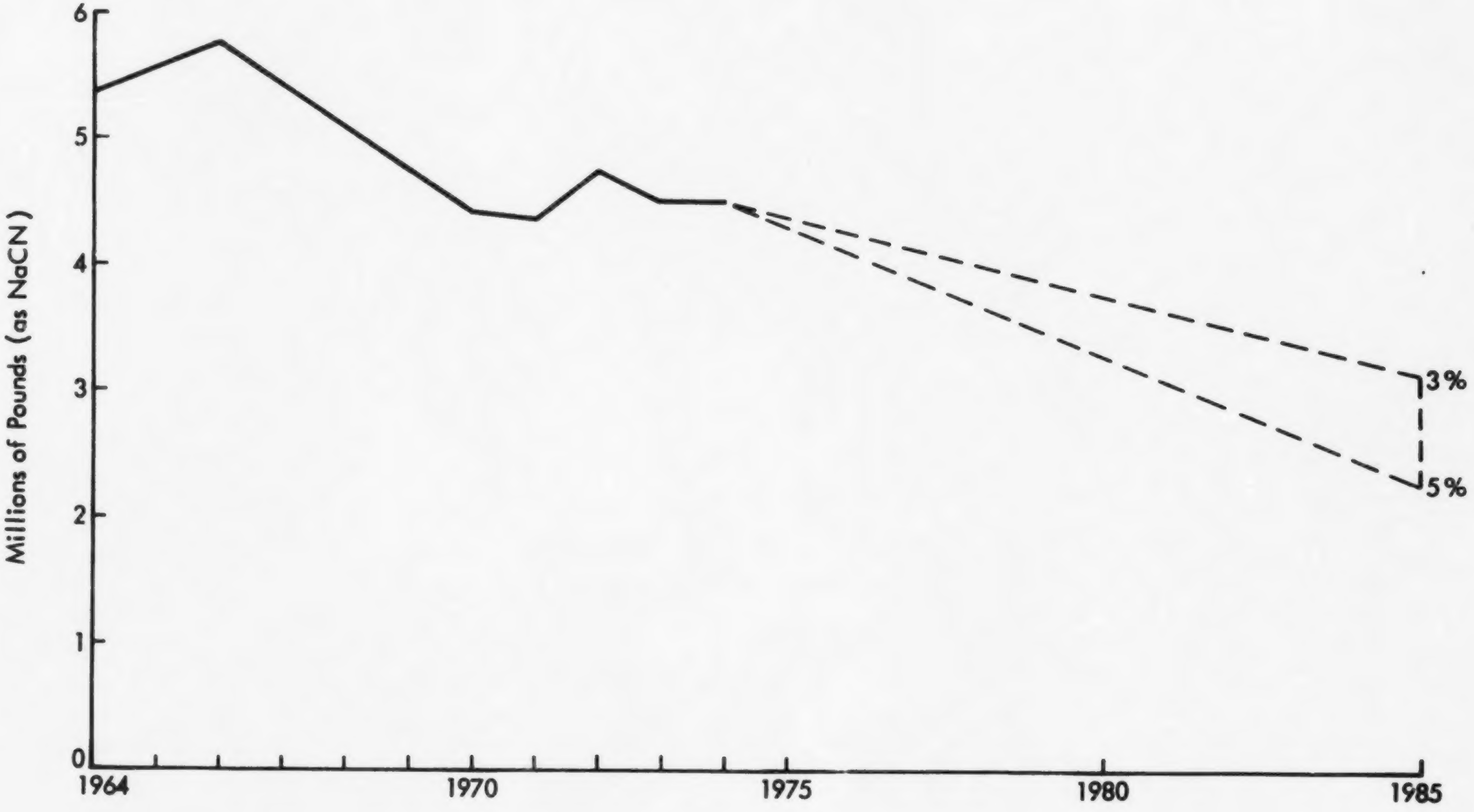

Figure 25. Estimated consumption of sodium cyanide for metal heat treating

Table 56. FACTORS INFLUENCING CONSUMPTION OF NaCN FOR METAL HEAT TREATING

Factor	Influence	Comments
Environmental concern	--	
Work hazards	--	To comply with OSHA standards[12]
Disposal, treatment costs	-	
Noncyanide salts	+	Require more attention[13]
Overspecification	+	Parts may not require case hardening
Cyanide advantages	+	Better case depth control, faster
Experience	+	Cyanides have been used for several years
Salt costs	+	Presently cheaper than noncyanide salts[10]
Energy shortage	+	Natural gas may be used in place of cyanide

For our purposes in describing the use of cyanides in photoprocessing chemicals it is important to focus on the silver image in the emulsion. Color processing of films involves "bleaching-out," or removing the original silver image. The resulting color negative or positive image contains essentially no silver, only the color dye images. All silver bleaches are solutions of oxidizing agents which convert the metallic silver to soluble silver compounds.

Among the most widely used bleaches are those based on ferricyanide and bromide; e.g., the solution may contain 10% by weight of potassium or sodium ferricyanide and 5% by weight of sodium bromide. Most bleaches contain buffers to keep the pH value of the solution between 5 and 10. Strongly acidic solutions are avoided since ferricyanide tends to be unstable in acids. Typical compositions of bleach solutions containing ferricyanide and bromide are given in Table 57.[1,2]

The starting point in any study of the manufacturers of such color processing chemicals is Eastman Kodak Company of Rochester, New York, which manufactures an estimated 75 to 85% of all color photochemicals in use today. Table 58 indicates the estimated market share of photochemicals.

Table 57. COMPOSITION RANGE OF BLEACH SOLUTIONS

Sodium or potassium ferricyanide	50 to 170 g/liter
Sodium or potassium bromide plus other chemicals to stabilize, buffer, or harden, etc.	10 to 30 g/liter

Table 58. PHOTOGRAPHIC CHEMICALS MANUFACTURERS

Company	Location	Market share (%)
Eastman Kodak Company	Rochester New York	75-85
Philip A. Hunt Chemical Corporation	Palisades Park, New Jersey	10-15
Agfa Gevaert, Inc.	Teterboro, New Jersey	≤ 5-10
Minnesota Mining and Manufacturing Company	St. Paul, Minnesota	
General Aniline and Film Corporation	Binghamton, New York	
Ilford and others	Paramus, New Jersey	
Total		100

These figures are rough estimates only.[1] Exact market information is lacking. Each of the above companies formulates photoprocessing chemicals, but only Eastman Kodak manufactures ferricyanides. American Cyanamid Company manufactures ferrocyanides for resale to formulators. The Hunt Chemical Corporation has in the past imported ferro- and ferricyanides for photoprocessing formulations and resale. Production and capacity data are considered proprietary information. The capital value of ferro-ferricyanide formulations is unknown.

Table 59 presents estimated annual consumption of sodium and potassium ferro- and ferricyanides in photographic processing chemicals. The estimates are approximations only and are subject to a deviation of approximately ± 20%. An assumed annual growth rate of 5% for the years 1965 through 1970 accounts for the rise in ferro- ferricyanide usage.

Table 59. ESTIMATED ANNUAL CONSUMPTION OF SODIUM FERROCYANIDE AND SODIUM FERRICYANIDE IN PHOTOGRAPHIC PROCESSING[3,4]

Year	Sodium ferrocyanide	Potassium ferricyanide	Total (million lb)
1965	0.8	3.2	4.0
1970	1.0	4.0	5.0
1975	0.5	2.0	2.5
1980	0.25	1.0	1.25
1985	0.2	0.8	1.0

The estimate of 5 million pounds in 1970 of ferro- and ferricyanides is by Alletag.[3] The subsequent decline in consumption of these chemicals is the result of economic regeneration processes which are available to photoprocessors and the increasing use of an alternate bleach reaction not using ferro- ferricyanides.

Photographic processing of color TV film and general photofinishing of amateur color films takes place throughout the U.S., whereas color motion picture processing is concentrated in southern California (greater Los Angeles area), the New York City-New Jersey metropolitan area, and, on a somewhat smaller scale, the metropolitan Chicago area. There are scattered independent photoprocessing laboratories and captive facilities in every city of approximately 200,000 or greater population. Television studios are an example of captive photoprocessing facilities. The total number of photofinishers, TV studios, and motion picture laboratories is probably near 2,000.[4] The industry is quite diffuse and data on the size, distribution, and geographic locations of the various processes are largely unknown to other than major film manufacturers. Some idea of the distribution of commercial photoprocessing laboratories can be obtained from the Sustaining Membership of the Society of Motion Picture and Television Engineers and the Society of Photographic Scientists and Engineers.

Three typical film processing laboratories located in Washington, D.C.; San Fernando, California; and Kansas City, Missouri; were contacted regarding ferricyanide consumption. The estimated consumption data are given in Table 60.

This average consumption may represent 0.1% of the total ferricyanide consumption by all photoprocessing laboratories. Thus, the total consumption may be of the order of 1.5 million pounds of ferro-ferricyanide. This particular consumption figure is an "educated guess" but is instructive. The proposed consumption figure given in Table 59 is 2.5 million pounds of ferro- and ferricyanide for the year 1975.

Table 60. FERRICYANIDE CONSUMPTION IN THREE TYPICAL FILM PROCESSING LABORATORIES

Company	Location	Annual ferro-ferricyanide consumption (lb)
A	Washington, D.C.	3,500
B	San Fernando, California	700
C	Kansas City, Missouri	200
Average		1,500

Environmental management by photoprocessing laboratories, TV stations, captive processors, etc., usually involves repeated regeneration of the spent ferricyanide bleach solutions, wherein relatively large amounts of ferrocyanides are present, and eventual disposal of the solutions.[5/] Disposal is uneconomical but occurs when a tank of processing chemicals has become contaminated, springs a leak, or has drifted so far out of chemical balance that regeneration is no longer possible. Disposal is generally by flushing into municipal systems witx large quantities of water. Parenthetically, some chemical losses occur spontaneously through drag-out or carry-over of the solutions through normal operations of passing the film through the processing solution. This carry-over is diluted with wash water which is largely recycled but is eventually disposed down the drain. Drag-out losses are kept to a minimum by use of squeegees and probably amounts to only 1% of the solution volume. Disposal and drag-out losses are kept at a minimum throughout the industry for economic as well as environmental reasons.[6/]

Potassium ferricyanide is a somewhat expensive chemical and several methods have been proposed to regenerate the exhausted solution. Each method involves oxidation of ferrocyanide to the active ingredient, ferricyanide. The three most prevalent methods of regeneration today are persulfate oxidation followed by bromite oxidation and ozonation. Other methods involve peroxide, permanganate, or electrolytic oxidation. Persulfate oxidation probably accounts for 70% of all regeneration processes.[1/] Regeneration has caused a significant decline in overall ferro- and ferricyanide consumption in photoprocessing chemicals.

Hendrickson has compared regeneration and disposal costs by various techniques.[7/] The results of this comparison are given in Table 61.

Table 61. COMPARATIVE REGENERATION AND DISPOSAL COSTS OF VARIOUS TECHNIQUES

Bleach treatment method	Cost or saving ($/gal including estimated material and labor)
Precipitation with iron as iron blue	-0.30
Persulfate regeneration	+0.75
Collecting and hauling away bleach	-0.54
Ozone regeneration	+2.05

These cost figures neglect capital investment, which is substantial in the case of an ozonation unit. The estimated cost of ozonation equipment is given in Table 62 according to Bober and Dagon.[8]

Table 62. ESTIMATED COST OF OZONATION EQUIPMENT (four processing machines)

10 lb/day ozone generator	$12,000
Automatic pH control unit and acid pump	700
Sparger system, tanks, plumbing	2,000
Ozone detection device	1,000
Connection to exhaust system	1,000
Installation and assembly	1,000
Conversion to automatic 24-hr operation	1,000
Total	$18,700

ANTI-CAKING AGENTS (3.1%)

Sodium ferrocyanide and iron blue are used as anti-caking additives in various salt mixtures for highway de-icing. Current practice utilizes approximately 0.2 to 0.5 lb of sodium ferrocyanide decahydrate and 0.1 to 0.2 lb of iron blue per ton of highway de-icing salt. The latter is principally sodium chloride to which is added calcium chloride in a ratio of approximately 95:5 by weight, respectively.

The estimated total amount of highway de-icing salt used in the winter of 1966 to 1967 was approximately 6.5 million tons, and it is assumed current usage is approximately the same. The cyanide additions amount to 1.3 to 3.2 million pounds of sodium ferrocyanide and 0.6 to 1.3 million pounds of iron blue annually. This is equivalent to 0.8 to 2.0 million pounds of NaCN and 0.6 to 1.3 million pounds of NaCN, respectively, for a total NaCN equivalent of 1.4 to 3.3 million pounds or 2.5 million pounds of NaCN as an annual average.

An EPA environmental impact study was completed in June 1971 outlining the use and environmental factors related to highway de-icing agents and additives.[1/] The above quantitative data were obtained from the EPA report and were updated by contacting the Salt Institute in Alexandria, Virginia, which supplied current application rates of cyanide additives.[2/] Further details regarding the runoff for ferrocyanides and iron blue as anti-caking agents in highway de-icing agents may be found in this EPA document.

No change in the general usage of sodium ferrocyanide and iron blue as anti-caking agents for de-icers is anticipated to 1985. Further, the application rate has probably stabilized since 1970 and no change to 1985 is expected.

AGRICULTURAL AND PEST CONTROL CHEMICALS (0.6%)

In past years two cyanides, liquid hydrogen cyanide and calcium cyanide, have been employed extensively in agriculture as insecticides, fumigants, and rodenticides. However, these uses have largely been superseded by synthetic insecticides and rodenticides or by volatile chlorinated hydrocarbons because of economic and safety reasons.

The principal company marketing cyanides for agricultural purposes and pest control purposes has been American Cyanamid Company, Agricultural Chemicals Division, Wayne, New Jersey, which supplied hydrogen cyanide and imported large amounts of calcium cyanide from Canada. The latter material, often called "black cyanide," is marketed as flakes, powder, or in block form under several trademarks, Aerocase, Cygon, Cyanogas, Cyano-A-Dust, Cyano-G-Fumigant, etc.

Exact consumption figures for cyanides as an agricultural and pest control chemical are unknown, but it was never a significant quantity, even during the grain surplus years. The use of hydrogen cyanide for this purpose has been discontinued and is not anticipated again unless grain surpluses return. Estimated consumption of calcium cyanide and hydrogen cyanide for agricultural purposes is given in Table 63.

Table 63. ESTIMATED CONSUMPTION OF CYANIDES FOR AGRICULTURAL AND PEST CONTROL PURPOSES[1,2]

Year	Million pounds $Ca(CN)_2$ annually
1965	2
1970	1
1975	0.5
1980	Nil[a]
1985	Nil[a]

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[a] If grain surpluses are again present, consumption could return to 1 to 2 million pounds annually.

Sources: American Cyanamid Company, Private Industry Sources, MRI Estimates.

Sources at American Cyanamid Company admitted this area was highly profitable, but was never large and did not represent a truly significant portion of the Agricultural Chemicals Division business volume.

Liquid hydrogen cyanide was dispensed by a small number, approximately 10, of specially trained persons authorized by American Cyanamid Company to fumigate grain elevators and storage bins in the 1950's and the 1960's. This activity principally related to the large grain surpluses held under U.S. government supervision. This practice was finally abandoned about 5 years ago when the grain surpluses disappeared.[1]

Hydrogen cyanide was used for many years as a fumigant for tobacco, cotton, and other imports, for citrus fruit, for tobacco seedlings against soil nematodes, and for general greenhouse use. Tree fumigation was accomplished by spreading a tent over the tree and releasing a predetermined amount of cyanide from a cylinder of liquid hydrogen cyanide.

Hydrogen cyanide is still used to a very limited extent as an agricultural fumigant. It is estimated that 50,000 to 60,000 lb of liquid HCN are used annually. The liquid HCN is obtained from E. I. du Pont de Nemours and Company and is repackaged in small steel cylinders by the Fumico Company of Amarillo, Texas. Fumico Company than acts as a distributor-retailer to trained persons who actually apply the liquid hydrogen cyanide for fumigation purposes, principally for imported goods and citrus.[2]

Fumico Company plans to market the HCN as a discoid of pressed porous wood impregnated with liquid hydrogen cyanide. The discoid would be about 3 to 4 in. in diameter and 1/8 to 1/4 in. thick. Several discoids would be placed in a steel container and the fumigation operator would, using appropriate protection, open the container and take out one or more discoids and place these strategically for maximum fumigation effect. After treatment, the discoids would be retrieved.

Orchard fumigation has also been accomplished by spraying with refined petroleum oil or by use of malathion (O-O-dimethylphosphorodithioate of diethyl mercaptosuccinate). A case study of malathion is contained in an EPA report.[3]

Other chemical fumigants used in the past have been Lindane (hexachlorobenzene) and methyl bromide. Both these substances are covered in EPA reports.[3,4]

Present solid fumigants include Phostoxin and Detia GAS-EX-B which are aluminum phosphides in a paraffin base. The active ingredient is phosphine gas, PH_3, which is released by hydrolysis of aluminum phosphide.

Present liquid fumigants include mixtures of carbon tetrachloride and carbon disulfide, generally in a ratio of 80 to 20 parts by volume. Other chlorinated or brominated hydrocarbons, ethylene dichloride or ethylene dibromide, may be added to this mixture.[5]

The principal manufacturers of these materials are given in Table 64.

In the area of general pest control, including rodents, either liquid hydrogen cyanide or calcium cyanide (flake, powder or bait) has been extensively used. Calcium cyanide was a convenient product to dispense and slowly released hydrogen cyanide gas when in contact with moist air. At present, American Cyanamid Company has a very small market in agricultural cyanides and pest control chemicals and may abandon this sector in the near future.[1]

A new use for sodium cyanide (and presumably calcium cyanide) has been proposed by the EPA in 1974 for coyote, fox, and other predatory animal control. An experimental use permit was approved for Texas for coyote control in April 1974.[6] The proposed method of application was the "M-44 Coyote Getter," a spring-loaded gun that shoots a cyanide charge into any animal that tugs at the bait attached to the gun.[7]

Table 64. PRINCIPAL MANUFACTURERS OF FUMIGANTS

Fumigant	Principal manufacturer	Location
Carbon disulfide	Stauffer Chemical Company	Delaware City, Delaware; Le Moyne, Alabama
Carbon tetrachloride	E. I. du Pont de Nemours and Company, Inc.	Corpus Christi, Texas
Detia GAS-EX-B	Chemische Fabrik Company	Laudenbach, West Germany
	Dist. by Research Products Company	Kansas City, Missouri
Ethylene dibromide	Ethyl Corporation	Magnolia, Arkansas
Ethylene dichloride	Shell Chemical Company	Deer Park (Houston), Texas
Lindane (HCB)	Stauffer Chemical Company	Louisville, Kentucky
Malathion	American Cyanamid Company	Warners, New Jersey
Methyl bromide	Dow Chemical Company, USA	Midland, Michigan
Phostoxin	Degesch Company	Frankfort, West Germany
	Dist. by Phostoxin Sales, Inc.	Alhambra, California

The experimental program has been expanded to the degree that the U.S. Department of the Interior was issued an experimental use permit by the EPA covering the period September 2, 1975 to September 2, 1976. The permit allows the use of 1,500 liters of a 33% sodium cyanide solution in up to 3,000 collars to be placed on tethered lambs. Other information relevant to restrictions on the use of the device, safety regulations, and geographic locations were included in the permit.[8]

The program as described will not be economically significant in any event. Environmental and safety hazards are of primary concern. Safer alternate chemicals are available for predatory animal control, e.g., nonfatal repellents and emetics such as lithium compounds.

Small animal pest control is presently accomplished by use of commercially formulated substances which contain warfarin, an anticoagulant, as the active ingredient. Warfarin is 3-(α-acetonylbenzyl)-4-hydroxycoumarin, and the sodium salt is marketed under a series of trade names as: Marevan, Prothromadin, Tintorane, Warfilone, Waran, etc. Manufacturers are listed in Table 65.

Table 65. PRINCIPAL MANUFACTURERS OF WARFARIN-TYPE RODENTICIDES

Manufacturer	Location
Velsicol Chemical Corporation	Chicago, Illinois
Stephenson Chemical Company	College Park, Georgia
Prentiss Drug and Chemical Company	Newark, New Jersey
The J. J. Dill Company	Kalamazoo, Michigan

Warfarin has been quite successful over the last 25 years as a rodenticide, but recently tolerance in rodents, lessening warfarin effectiveness, has spread.

Other pest control chemicals have included DDT as a "tracking powder" against mice, arsenious oxide, sodium fluoroacetate or "1080", strychnine sulfate, and zinc phosphide.

Rohm and Haas Chemical Company has developed a rat poison based on carbamates, a well-known class of insecticides. The new rodenticide has the advantage of broad-spectrum activity against rodents, single-dose effectiveness, and is relatively innocuous to other animals.[9]

The total market potential for rodent control represents about $8 million annually in chemical raw materials, $15 to $20 million at the wholesale level, and $30 to $40 million at the retail level. The world market is estimated at more than $100 million annually.[10]

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CHAPTER VIII

CYANIDE TREATMENT METHODOLOGIES

Much has been written concerning cyanide effluent treatment, principally in the metal finishing sector. All techniques to be discussed are applicable to cyanide waste effluents. Metal finishing wastes are much more difficult to treat than simple cyanide wastes because of the presence of heavy metals, organic brighteners, and other proprietary additives.

Several EPA development documents for guidelines are included in the bibliography together with other pertinent references to effluent treatment. This information is readily available and is well known within the industry. This report will bring together all the treatment methodology that is known in a summary form and present a current evaluation of these for an overview of cyanide effluent treatment.

A list of various treatment techniques for cyanides includes, but are not limited to, the following:1/

Destructive Techniques

1. Destruction of cyanide by alkaline chlorination, including the use of hypochlorites for dilute solutions (batch or continuous).

2. Destruction by electrolysis for concentrated solutions (batch).

3. Destruction by ozonation with/without ultraviolet radiation (batch).

4. Kastone Process (Du Pont) using hydrogen peroxide and formalin (batch).

5. Destruction by hydrolysis at an elevated temperature (batch or continuous).

6. Cyanide removal by activated carbon adsorption (batch or continuous).

Recovery Techniques for Metal and Cyanide Values

1. Reverse osmosis (batch or continuous).
2. Ion exchange (batch or continuous).
3. Precipitation of heavy metals (batch).
4. Evaporative recovery (batch or continuous).

Engineering Methodologies

To these techniques the following engineering methodologies should be added:

1. Countercurrent rinsing (cascade rinsing).
2. Integrated chemical rinse systems.
3. Effluent segregation.

The relative proportion of plating establishments using the above destruction and recovery cyanide techniques is as follows:[2]

Alkaline chlorination	~ 90%
Electrolysis	~ 1%
Ozonation	~ 1%
All others	~ 8%
	100%

The popularity of alkaline chlorination including the use of hypochlorite is due to the dependability, ease of operation if properly engineered, and the efficiency of cyanide destruction to very low levels, ≤ 0.1 mg/liter.

Essentially, all metal finishing facilities employ one or more of the above mentioned effluent handling methodologies. Effluents are no longer combined and treated in total because of potential increased complexity of the resulting solution, increased chemical costs to destroy additional organic materials in the effluent, and the loss of any recovery possibility of specific chemicals.

DESTRUCTIVE TECHNIQUES

Alkaline chlorination is used to treat approximately 90% of cyanide effluents on an industrywide basis. Capital investment costs for chlorine gas storage, handling and metering are significant. Chemical costs, including caustic and chlorine gas, are considerable on a continuous basis. However, the system does work well and, when properly installed, is dependable. Holding tanks and lagoons are necessary for handling the resulting metal sludges of hydrated heavy metal oxides.

Cyanide ion is oxidized to cyanate ion or to carbon dioxide and nitrogen gas depending on the chlorination conditions. Thus, with chlorine gas the following reactions may occur:

$$NaCN + Cl_2 + 2NaOH \longrightarrow NaCNO + 2NaCl + H_2O$$

and/or

$$2NaCN + 5Cl_2 + 12NaOH \longrightarrow N_2 + 2Na_2CO_3 + 10NaCl + 6\ H_2O$$

A toxic intermediate compound, cyanogen chloride gas, CNCl, is formed but a pH value of 10.5 or higher causes the cyanogen chloride to be rapidly transformed to cyanate ion which is one-thousandth as toxic as cyanide or cyanogen chloride. Usually 20 min are allowed for the reaction to continue if heavy metal cyanides are present. These materials are more difficult to oxidize than sodium or potassium cyanide. Some heavy metal cyanides are essentially unchanged by alkaline chlorination, e.g., ferri- and ferrocyanide, hence the distinction of "cyanides amenable to chlorination" is made.

The final oxidation stage to nitrogen and carbon dioxide proceeds rapidly at pH 7.5 to 8.0 in 10 to 15 min, but at pH 9.0 to 9.5 the reaction is slow. The processes utilize one or more holding tanks to accomplish the oxidation and at the same time allow for sludge formation of hydrated metal oxides.

Alternatively, sodium or calcium hypochlorite may be used as a solid or as a solution to destroy cyanide. The oxidation may proceed to cyanate or to completeness as indicated previously.

$$NaCN + NaOCl \longrightarrow NaCNO + NaCl$$

and/or

$$2NaCN + 5NaOCl + H_2O \longrightarrow N_2 + 2NaHCO_3 + 5NaCl$$

The process is simpler than with gaseous chlorine and the hypochlorite needs no additional caustic. Agitation is essential for efficient conversion. Costs of capital equipment are less with hypochlorite, but chemical costs are higher. It is believed that the hypochlorite treatment technique is more applicable to smaller plating shops. In either case, effluent cyanide levels can be as low as ≤ 0.1 mg/liter. Direct dischargers in some states, e.g., Pennsylvania, are held to 0.02 mg/liter cyanide amenable to chlorination.[2/]

Electrolytic decomposition of cyanide wastes can be effective, but works best for higher cyanide concentration levels such as in spent plating baths at 45,000 to 100,000 mg/liter. The method is inefficient for cyanide in rinse waters. The time factor for complete destruction may extend from 7 to 21 days, depending on the initial cyanide level, and the final cyanide level may be in the range 0.1 to 0.4 mg/liter. It is probably better to treat only the higher concentration levels to an intermediate level, 500 to 1,000 mg/ml, and then utilize chlorination. Metal recovery may be easier by electrolysis, since electrodeposition may occur, and this can reduce overall operating costs. The electrolysis technique is used only for ~ 1% of cyanide treatment techniques.

Ozonation with and without ultraviolet radiation is an attractive alternative for cyanide destruction, but is performed ~ 1% of the time at present. Heavy metal cyanides are essentially resistant to direct ozonation.

At least one company, PCI Ozone Corporation of West Caldwell, New Jersey, markets an ozonation system for cyanide wastes. Houston Research, Inc., of Houston, Texas, is proposing the combination ozonation-UV illumination system.

PCI installed the first ozonation system for an industrial plant at the Sealectron Corporation at Mamaroneck, New York, in February 1974. The project was undertaken and financed in part by an EPA demonstration grant. The cyanide effluent contained 60 ppm cyanide, 32 ppm Cu, and 3.4 ppm Ag. It was treated with 1 to 1-1/2% ozone in air. After ozonation, the effluent was mixed with acid plating waste containing 14 ppm Ni, 2 ppm Sn, and 0 to 8 ppm Pb. Cyanide in solution was not detected. The previous metals were precipitated as hydrated metal oxides. It is not stated if any cyanides which might have escaped ozonation were in the sludge.[3/]

The combination of ozonation and ultraviolet radiation is quite effective against resistant heavy metal cyanides. Ferricyanides may be reduced to 0.1 mg/ml in 20 min at 150°F with a 5% ozone concentration in air and with 16 watts of UV illumination. This system is being readied for market by Houston Research, Inc., and is undergoing a series of field tests at various installations in the U.S. and France.[4/]

E. I. du Pont de Nemours and Company markets a cyanide waste treatment system (Kastone process) utilizing hydrogen peroxide, formalin, and a metal salt (usually magnesium sulfate) which converts cyanides to cyanates and other compounds of organic acids, e.g., glycollates. For zinc cyanide wastes the cyanide level is generally 0.1 ppm and the hydrated zinc oxide is settled, filtered, and can be recycled to the plating bath.[5]

Hydrolysis of cyanide solutions at high pressure and elevated temperature converts metal cyanides to ammonia and formate. Typical conditions involve holding the cyanide solution at 150 to 200°C for 5 to 10 min in steel reactors. The resulting solution contains ~ 4 mg/liter cyanide ion as compared to alkaline chlorination or the Kastone process which is capable of attaining reductions of cyanide to ≤ 0.1 mg/liter. Transition metal cyanides require longer retention times and/or higher pressures and temperatures.[6]

Cyanide can be adsorbed on activated charcoal and the associated metal recovered. For example, zinc cyanide can be adsorbed on carbon with 99% cyanide removal. Recovery of the zinc is accomplished by passing dilute acid through the charcoal column, producing soluble zinc ion and hydrocyanic acid. Pilot-plant operations conducted at Battelle Memorial Institute indicated feasibility of metal finishing waste treatment by this process.[7]

Cyanides can be oxidized after adsorption on activated charcoal.[8] Thus, when a copper cyanide solution containing dissolved oxygen is passed through an activated charcoal column, the cyanide radical is oxidized to cyanate. The cyanate in the presence of copper is hydrolyzed to bicarbonate ion and ammonia. The net result is that cyanide is converted to bicarbonate or carbonate and ammonia and the copper precipitates on the granular carbon as copper carbonate.

The system fails with solutions of cadmium or iron cyanide but is partly successful for zinc cyanide. The differences in effectiveness are due to differences in the metal cyanide complex bond strengths.

Cyanide effluent levels are of the order of 0.1 mg/liter. The copper can be recovered and the carbon regenerated. Cost estimates for alkaline chlorination versus catalytic carbon adsorption and oxidation (catalytic oxidation) are given in Table 66.

RECOVERY TECHNIQUES

Reverse osmosis (RO) is a technique of potentially great importance since it offers recovery rather than destruction with chemical cost savings.[9-11] The concentrate of metal salt and cyanide obtained by RO can be returned to the plating bath and the alter-effluent can be returned to

Table 66. DIRECT CHEMICAL COST COMPARISON ALKALINE CHLORINATION VERSUS CARBON CYANIDE REMOVAL[8]

A. Cost basis[a]

Flow - 25 gal/min, 24 hr/day, 5 days/week
[CN] - 100 mg/liter 30 lb/day

Cyanide destruction catalyst 25¢/lb - 25% active
Oxygen (industrial) - 244 ft^3 cylinders - 16¢/lb
Liquid chlorine (150 lb cylinder) - 11.5¢/lb
Liquid caustic (50% NaOH - 55 gal. drum) - 13¢/lb

B. Feed rates

Alkaline chlorination -

Chlorine to cyanide - 10:1
Caustic to cyanide - 6:1

Catalytic oxidation -

Catalyst:cyanide:oxygen - 1:1:1

C. Estimated direct chemical costs

Complete destruction -

Catalytic oxidation - $1.25/lb [CN][b]
Alkaline chlorination - $1.93/lb [CN]

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[a] Cost figures are averages for 1972.
[b] Includes carbon change once per year. After start-up, cost may be reduced to $1.00/lb.

the rinse cycle in principle. Field demonstrations have been conducted to identify problem areas and to test membranes and equipment on actual cyanide plating wastes.[12/] The difficulty is that membranes able to withstand high alkalinity and high pressures are not available at present, thus RO application to cyanide wastes is awaiting the development of suitable membrane materials.

A recent experimental program using ion exchange has been reported by Rohm and Haas Company wherein a cyanide waste stream is treated with ferrous sulfate at pH 8 to 11. After the resulting sludge of ferrous hydroxide is removed by filtration or flocculation, the resulting ferroxyanide solution is absorbed onto a weakly basic ion exchange resin. Once loaded with the ferrocyanide, the ion exchange resin is regenerated with dilute NaOH resulting in a stream of ferrocyanide. The latter material can be disposed of by a number of methods, none of which is totally satisfactory: preparation of iron blue, concentration and incineration, or landfill, etc.[13/] This technique is new, but is posing additional environmental concern in view of the photodecomposition of the leachable iron cyanides and the potential release of toxic hydrogen cyanide.

Recovery of metal from cyanide effluents can also be accomplished by the so-called waste-plus-waste (WPW) process developed at the Bureau of Mines, Rolla, Missouri.[14/] Various acid and alkaline cyanide wastes were combined to completely precipitate the metals and cyanide as metal cyanides and hydrated metal oxides. The metals and the cyanides can be recycled. Common metals from electroplating wastes, including zinc, copper, and cadmium, were successfully treated. Free cyanide ions in the resulting filtrate was ≤ 0.03 mg/liter. Only small amounts of HCN were detected during neutralization.

Figure 26 presents a possible WPW recovery process for silver wastes. The recovered silver was 99.1% pure and contained 0.03% Cu and < 0.001% Ni and Fe.

The WPW process may find use in industry as an inexpensive first step to remove cyanides and most metals from effluents. Provision for control or incineration of possible hydrogen cyanide evolution is mandatory. After precipitation of the metals and cyanide, other more conventional treatment techniques could be applied.

ENGINEERING METHODOLOGIES

Much of the operating expense of waste treatment can be reduced by using cascade or countercurrent rinses, concentrating the drag-out chemicals and recycling them. A second technique which lowers costs is the

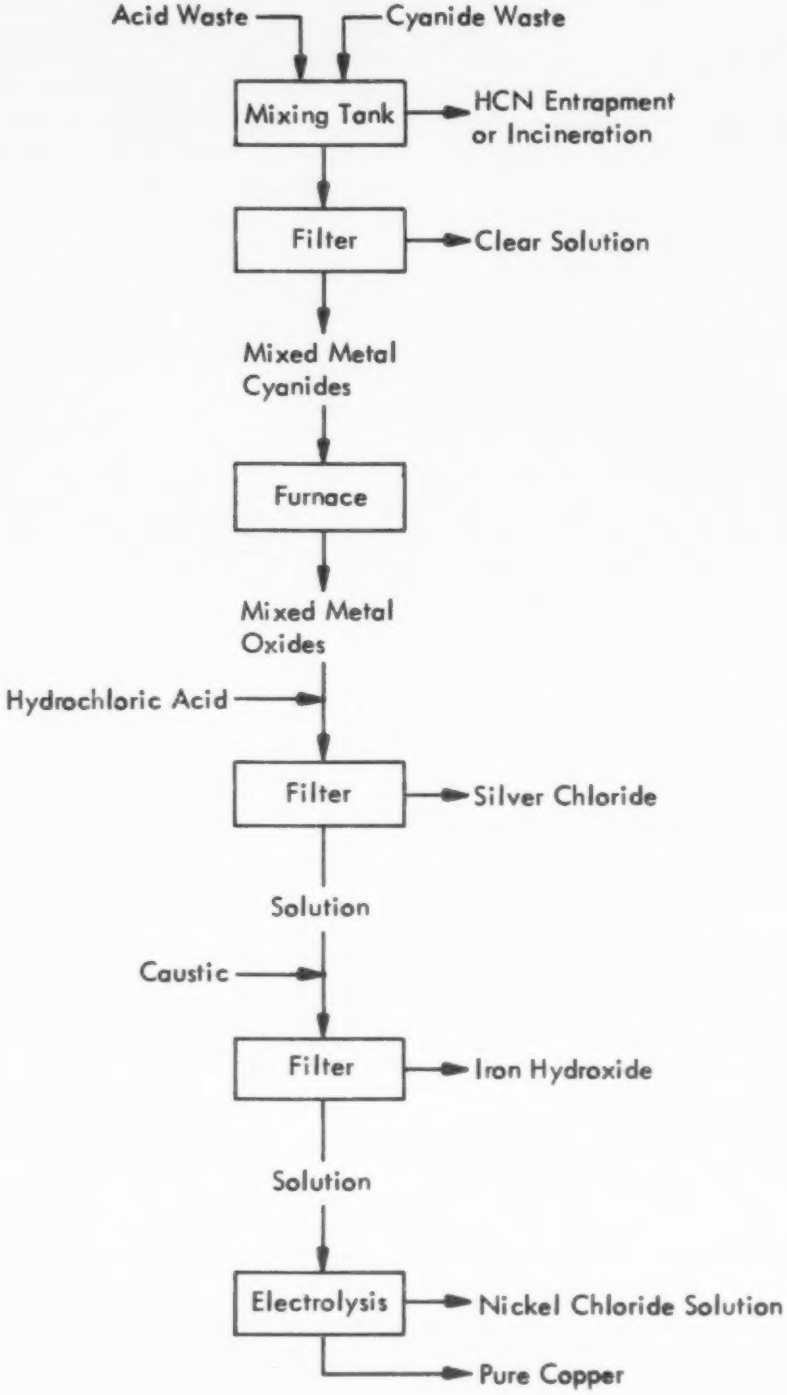
Acid Waste
Cyanide Waste
Mixing Tank
HCN Entrapment or Incineration
Filter
Clear Solution
Mixed Metal Cyanides
Furnace
Mixed Metal Oxides
Hydrochloric Acid
Filter
Silver Chloride
Solution
Caustic
Filter
Iron Hydroxide
Solution
Electrolysis
Nickel Chloride Solution
Pure Copper

Figure 26. Possible WPW process treatment for metal-cyanide wastes

integrated treatment system wherein chemical rinses are employed to chemically treat the cyanide drag-out during the rinsing operation. Each technique has the advantage of simpler and more economical treatment procedures since the volume of water is lower and the treatment is applied to the source rather than to a complex total-waste stream.

Countercurrent rinsing techniques are those wherein fresh water enters a second rinse tank, overflows into the bottom of the first rinse tank after the plating bath and thence flows to a treatment or recovery system. In this manner, the last rinse tank is insured of clean water without excessive contamination from a preceding rinse tank. Each additional rinse tank through which water flows, allows a reduction in water usage by a factor of 10 or somewhat less. Fresh water costs have been shown to be a major cost factor, particularly for electroplating rinsing and waste treatment.[15/]

The integrated treatment system can be part of a self-contained closed-loop system in which the chemical rinse stations are enjoined to a reservoir tank. This has the advantage of reducing cyanide in the subsequent water rinse to a level < 0.02 mg/liter by simple dilution before discharge. Effluent guidelines prescribe average permissible levels and require knowledge of the total amount of cyanide released in a given time, i.e., volume x average concentration.

Evaporative recovery may be employed in conjunction with cascade rinsing for recovery of cyanide and metal values as an alternative to destruction and precipitation. Such a system is shown in Figure 27 which shows countercurrent rinsing in two tanks followed by a recovery-evaporation step wherein concentrated metal and cyanide salts are returned to the plating solution concentrate and the distillate is returned to the last rinse tank. This is a closedloop system with essentially no discharge except for accidental leakage, spills, bath contamination, etc.

EFFLUENT TREATMENT COSTS

Cost estimates for any plating recovery or destruction system must include the following considerations: capital investment, special monitoring apparatus, chemicals, modification of existing apparatus, fresh water, maintenance, treatment of concentrated solutions and/or sludges, hard water softening, pH adjustment, sewer rental charges, etc.

Many authors simply compare chemical costs, but the total of all costs is what is important. A small advantage in chemical costs may be overshadowed by a large capital investment or higher overall operating costs.

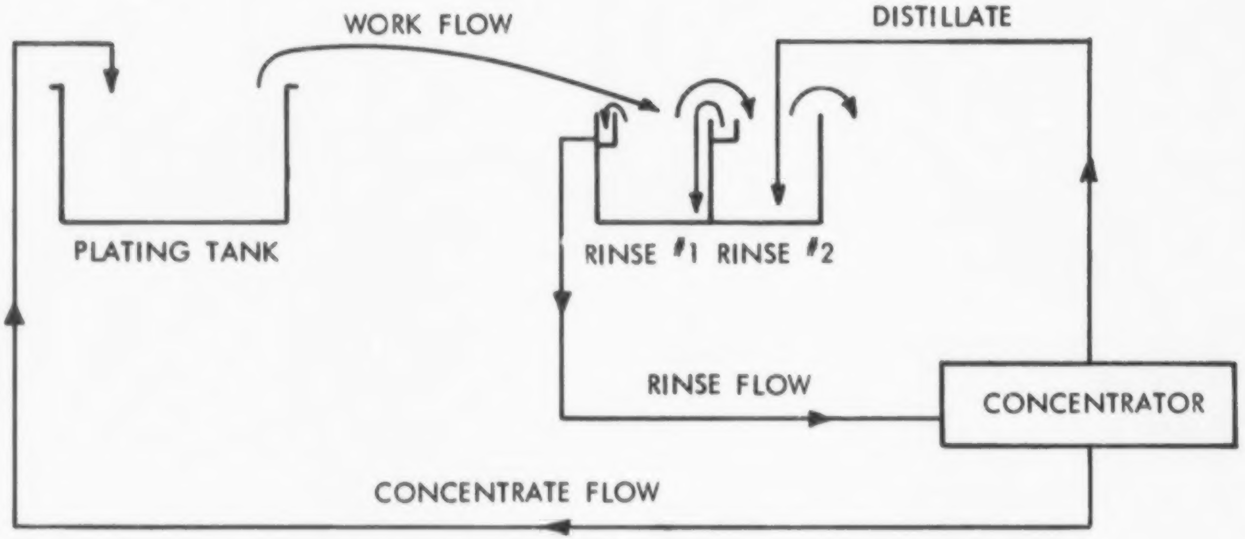
WORK FLOW
DISTILLATE
PLATING TANK
RINSE #1 RINSE #2
RINSE FLOW
CONCENTRATOR
CONCENTRATE FLOW

Figure 27. Closed-loop evaporative recovery system

A cost comparison for the above factors has been given by Lancy, Nohse, and Wystrach for three techniques: ion exchange, continuous treatment, and integrated treatment. The facility chosen for economic study consisted of two automatic plating lines which contained a cyanide copper strike, acid copper, double nickel, and chromium plating cycles.[15]

Ion exchange may remove the chemical content and allow reuse of rinse waters. Up to 80 to 90% of the rinse water may be recirculated for economical use of water. Hence, the total effluent volume is reduced.

Continuous instrumented treatment is based on continually sensing the flowing effluent stream and precipitating the metal salts by chemical treatment. Caustic chlorination oxidizes the soluble cyanides. The precipitates are settled in a clarifier to collect the hydrated metal oxides. This is followed by sludge concentration, dewatering, and drying.

Integrated waste treatment employs a chemical rinse following the plating step and prior to the work entering the second or later rinse tanks. Heavy metals are precipitated in the first tank and removed from the rinse water.

Table 67 presents a comparison of total treatment costs for ion exchange, continuous treatment, and integrated treatment. It is seen that the integrated treatment system yields a lower total cost annually.[15]

The most significant costs for metal finishing waste treatment for this plating facility are capital investment and amortization cost of installations, water cost, sewer rental charges, treatment of concentrates, and sludge-handling costs. Chemical costs are relatively minor. Environmental management of metal finishing effluents is a complex and difficult topic, and requires an engineering overview of all potential costs for each option. Merely focusing on chemical costs and ease of operation does not necessarily yield the most effective, trouble-free, and economical process.

Table 67. COMPARISON OF TREATMENT COSTS, $ (1972)

	Ion exchange	Continuous treatment	Integrated treatment
Fresh water	187	28,894	165
Ca, Mg precipitation of hard water salts	21	4,597	-
pH adjustment for oxidation-reduction control	-	4,367	-
Neutralization	-	2,784	79
Sewer rental charges	157	24,143	138
Deionized water	289	289	289
Treatment and concentration of solids and sludge handling	33,589	27,981	2,588
Electric energy	1,289	3,405	960
Chemicals	6,759	1,743	6,084
Wages	3,863	4,017	2,008
Amortization	31,091	16,966	4,809
Maintenance	3,999	12,767	1,443
Total cost annually	81,244	131,953	18,563

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CHAPTER IX

ALTERNATIVE MATERIALS, PROCESSES AND USES

In this chapter alternate raw materials and methods of production of cyanides are discussed. The presentation also includes alternative chemicals to cyanides in the various industrial sectors.

ALTERNATE RAW MATERIALS AND SYNTHETIC METHODS

The present methods of HCN manufacture by the Andrussow or the Degussa process seems to offer no immediate suggestions for alternate raw materials. Certainly HCN is the simplest cyanide to make and also the most versatile; offering easy access to either the organic or the inorganic sector. The present processes start with the simplest of materials; ammonia, methane, and air (absent in the Degussa process). Methane from natural gas could be in relative short supply in the distant future but there are alternates to methane production, e.g., cracking of crude oil.

Of course, each synthesis process could conceivably be made to operate better through use of a more efficient catalyst which would allow a lower reaction temperature, higher flow rates, a shorter contact time, etc.

The production of acrylonitrile at present is around 1.4 billion pounds annually which yields approximately 200 million pounds of HCN as by-product. If all the primary HCN plants across the country would cease production except the Rohm and Haas facility having a capacity near 180 million pounds, the total production of 380 million pounds would meet our current needs for HCN. Thus, a tremendous capacity exists far exceeding our present needs for HCN. This situation which combines overcapacity from two processes yielding HCN arouses little enthusiasm to seek alternate paths to cyanides today.

If a crisis in crude oil and/or natural gas does develop in the future, cyanides can be made by the time honored historical techniques described earlier in Chapter IV. The Bucher high temperature process which combines sodium carbonate, coke, and nitrogen in an iron vessel will yield sodium cyanide, another versatile chemical. The older Beilby process combining soda ash, carbon, and ammonia could be revived. The key is to manufacture either hydrogen cyanide or sodium cyanide; from these all other organic and inorganic cyanides can be made. Fortunately, there are many routes to these two fundamental cyanides.

ALTERNATES TO CYANIDES IN VARIOUS INDUSTRIAL SECTORS

In this section various substitute materials for cyanides are discussed. Some trend toward cyanide replacement because of waste treatment problems and costs has already been observed by industry spokesmen. A countertrend is also emerging which, in essence, holds that cyanides are so superior for certain industrial uses that the alternate materials are a poor second choice. Further, the substitute chemicals have potential waste effluent problems themselves. At least cyanides are well understood, the treatment technology is on a sound basis, and the treatment costs could conceivably drop in the near future as new technology is developed.

Metal Finishing

Zinc plating constitutes the largest plating sector in the U.S. today. With the advent of restrictions on cyanide effluents, much research and development has gone into development of mid-to-low-to-noncyanide zinc baths in the last 10 years. The noncyanide baths include acid chloride, acid sulfate, and fluoborate. Some plating baths substitute ammonia and/or chelating agents as zinc complexers instead of cyanide. Table 68 indicates the composition and estimated distribution of bright zinc plating baths in 1975 according to Geduld.1/

Table 68. ESTIMATED DISTRIBUTION OF ZINC PLATING BATHS BY TYPE

Zinc bath type	Cyanide concentration (g/liter as CN)	Estimated % of market
Regular cyanide	45	36
Mid-cyanide	15-45	25
Low-cyanide	3-11	15
Micro-cyanide	0.75-1.0	8
Noncyanide alkaline	0	7
Acid	0	9
Total		100

The shift to noncyanide zinc baths has largely been accomplished in small plating shops (60 to 80%) as the result of stringent effluent regulations coupled with general inability or reluctance of the small platers to invest heavily in treatment facilities for cyanides. The larger shops are still using cyanide zinc baths with effluent alkaline chlorination primarily and account for a very large fraction of all zinc plating. The larger shops have invested heavily in cyanide treatment equipment and monitor treatment expenses through careful accounting practices.[2]

Several companies are now heavily promoting noncyanide zinc processes. Among these are: Lea Ronal, Inc., Freeport, New York; R. O. Hull and Company, Inc., Cleveland, Ohio; the Udylite Company, Division of Metal Industries Corporation, Warren, Michigan; The Aldoa Company, Detroit, Michigan; and Conversion Chemical Corporation, Division of 3M Company, Rockville, Connecticut. One company, Lea Ronal, Inc., assisted Tracor, Inc., of Des Plaines, Illinois, in converting some 400,000 gal. of zinc plating bath to a noncyanide system for barrel plating. The changeover also included tin and cadmium plating lines and was accomplished over one weekend.[3]

The alkaline and acid bright zinc noncyanide plating baths are not without some compromises, however. Some baths are not as efficient, do not have the same throwing power, ease of operation and control, etc., as the historic cyanide bath which has the distinct advantage of some 100 years of development. Recent research has reduced these shortcomings through use of special organic brightening and leveling agents. It now appears acid bright zinc baths have a distinct advantage over alkaline baths as regards brightness, higher current efficiency, the option of direct plating on cast iron without intermediate deposits, etc.

Some noncyanide zinc baths utilize chloride, ammonia, or chelating agents in addition to organic wetting agents and proprietary brighteners. The presence of these materials in effluents may have deleterious effects themselves. For example, high concentrations of ammonia in an effluent may cause difficulty in subsequent treatment since ammonium ion can very effectively complex zinc, nickel, and copper, for example, and prevent precipitation of the hydrated metal oxide. Chelating agents, such as EDTA, complex zinc salts to such a degree that precipitation as zinc hydroxide from reuse waters is impossible at any pH range, the residual zinc concentration remaining near 20 mg/liter.[4] Ammonia in an effluent reacts with chlorine to form chloramines which are toxic to fish. In addition, the presence of ammonia increases chlorination costs during effluent treatment.

The zinc plating bath of the future may well be composed of zincate (zinc hydroxide dissolved in excess caustic soda), easily degradable chelates, nonionic wetting agents, and proprietary brighteners.

In the areas of alkaline copper, brass, and bronze plating there are no commercially available noncyanide processes as yet. Development in these areas is continuing. A noncyanide cadmium plating bath has been developed by Conversion Chemical Corporation for plating steel but has not received wide application.

Engelhard Industries markets a series of alkaline noncyanide gold plating baths covering varying degrees of deposit hardness. The bath properties appear to be equally as desirable as the traditional cyanide baths.

Cyanide-based silver plating baths have been the subject of many researchers since their discovery in 1840, but only in 1975 has a noncyanide bath become comercially available. The new, noncyanide silver bath is based on a derivative of succinic acid. Technic, Inc., of Providence, Rhode Island, markets the proprietary bath and has applied for patent rights. The technical reports claim high quality deposits with nearly the same costs as the traditional cyanide processes.

Finally, various noncyanide metal stripping, descaling, and cleaning solutions are available. Table 69 indicates the products currently available for use by metal finishers.

Table 69. PRODUCTS CURRENTLY AVAILABLE FOR USE BY METAL FINISHERS

Noncyanide solution	Source	Location
Nickel stripper	Enthone, Inc.	New Haven, Connecticut
Nickel stripper	MacDermid, Inc.	Waterbury, Connecticut
Brass detarnisher and burnisher	Frederick Gumm Chemical Company	Kearny, New Jersey

In summarizing it may be said that there are noncyanide processes commercially available for many metal finishing operations. What remains to be seen is whether or not they are equal to the task, are economical, and do not contribute effluent treatment problems of their own. These factors are important to metal finishers and the public alike.

Pigments

Substitutes for iron blue as paint and ink pigment have been developed in recent years. The current inorganic pigments for blue coloration in paints include cobalt blue, a mixture of cobalt, chrome, and aluminum oxides, and ultramarine blue, a complex sodium aluminum sulfosilicate.[1] These materials have poor hiding power (translucent) but are alkali resistant. Ultramarine blue is used in latex and alkyd resin-based paints and in automobile and agricultural implement enamels and finishes. Cobalt blue is used for pale tints and toning of white. Both of these pigments are more expensive than iron blue. Manufacturers of cobalt blue and ultramarine blue are given in Table 70.

Table 70. MANUFACTURERS OF COBALT BLUE AND ULTRAMARINE BLUE

Company	Location	Pigment
Chemetron Corporation	Holland, Michigan	Ultramarine blue
Frank D. Davis Company	South Plainfield, New Jersey	Cobalt blue
Ferro Corporation	Cleveland, Ohio	Cobalt blue
Hercules, Incorporated	Glens Falls, New York	Cobalt blue
Naftone, Incorporated	New York, New York	Cobalt blue
Sheperd Chemical Company	Cincinnati, Ohio	Cobalt blue
Whittaker, Clark and Daniels Company	South Plainfield, New Jersey	Ultramarine blue

Many of these companies also offered iron blue as a pigment in recent past years.

The environmental impact arising from substitution of cobalt blue or ultramarine blue is unknown at present. Chrome oxide is one of the components of cobalt blue and is environmentably undesirable as a waste product. Any contamination problems by cobalt blue would be more probable at the point of manufacture than at the final disposal at a municipal or county facility. Ultramarine blue appears to be innocuous, but no evidence is available to make a sound judgment.

Organic blue pigments include two general types: copper phthalocyanine blue and indanthrene blue. The former has excellent tinctorial power and heat and chemical resistance but is semitranslucent. It has been used in ink and textile manufacture and now increasingly for paint applications, particularly for coil coating and high-temperature operations.[2] In 1963, approximately 4.3 million pounds were produced domestically.[3]

Indanthrene blue is an anthroquinone derivative and is relatively expensive as is phthalocyanine blue. This material has good acid and alkali resistance and withstands temperatures up to 150°C.

A third group of dyes based on triphenylmethane and containing amino and sulfonic acid groups are represented by peacock blue and alkali blue. These have brilliant colors but poor alkali resistance and light-fastness. Other organic blue colors certified by the U.S. FDA are available as pigments for limited applications, e.g., FD&S Blue No. 6, Indigotin.

Manufacturers of these organic blue pigments include many of the former list for inorganic pigments plus others, e.g., E. I. du Pont de Nemours and Company, Wilmington, Delaware, and Ciba-Geigy Corporation, Ardsley, New York, etc.

The environmental impact of the various organic pigments is unknown but each could be incinerated easily. Only copper phthalocyanine offers any hint of environmental problems. This material is actually the copper salt of phthalocyanine, a porphyrin. It is unusually stable and can be sublimed at 550°C in an inert atmosphere without decomposition. Ultimate destruction of the porphyrin still leaves copper or copper oxide as a residue depending on the incineration technique employed.

Industry spokesmen indicate a future decline in iron blue consumption as pigment with phthalocyanine blue becoming more prominent in the paint and ink sectors. The advantages of phthalocyanine blue as paint pigment are related to its stability in alkaline media and its better heat resistance.[2/] The advantages as ink and textile pigment are related to its stability in acid and alkaline media, its cleaner shade, its higher tinctorial power, and its resistance to bleed of oils and solvents.[4/]

Mining Chemicals and Processes

Presently, cyanidation is the single most important method of recovery for gold, domestically. In discussing the alternatives to cyanidation, a brief description of the five processes currently employed to recover gold and silver is in order. The processes are outlined in Table 71.

Gravity concentration is used on gold occurring in a relatively coarse native state (occurring as metallic gold). This is generally descriptive of placer deposits, although some lode deposits are amenable to gravity concentration. In processes using gravity concentration, the gold would ultimately be recovered by amalgamation, smelting or cyanidation, and therefore the percent recovered in Table 71 is somewhat low. Very little gold production can be supported by gravity concentration alone. In conclusion, gravity concentration is not a viable alternative to cyanidation.

Table 71. PROCESSES FOR RECOVERY OF GOLD AND SILVER

Process	Use cyanides	% Gold recovered (1972)[1]
Gravity concentration	No	< 1
Amalgamation	No	< 1
Flotation	No	a/
Smelting	No	44
Cyanidation	Yes	55

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a/ Reported in Smelting.

Amalgamation can be used to recover native gold with no dependence on the size of the gold particles. Gold ores with a high percentage of slimes are not recovered by amalgamation as the losses of mercury and consequently gold are too high. Prior to 1971, approximately 25% of the domestic gold production resulted from amalgamation. However, due to environmental concern, amalgamation is currently limited chiefly to recovery of gravity concentrates in the processing of lode deposits. Like gravity concentration, amalgamation does not appear to be an alternative to cyanidation.

Flotation, as a method of recovery for gold, can be applied only to (a) gold occurring with tellurides, (b) when in solid solution with complex iron sulfides, or (c) when occurring with copper, lead and zinc sulfides (base metal ores). Flotation recovery of the telluride and complex iron sulfide-gold ores is not an important source of gold domestically and cannot be considered as an alternative to cyanidation. The flotation recovery of gold from copper, lead, and zinc production is important, but the gold is a by-product and therefore subject to the economics of recovery of the base metal. Likewise, by-product gold recovery cannot be considered as an alternative of cyanidation.

The recovery of gold by smelting is the second most important source of gold in the U.S. Recovery by smelting includes the gold produced by flotation of telluride and iron sulfide ores discussed in the previous paragraph. However, the majority of the gold produced by smelting is derived as a by-product from the smelting of copper, lead and zinc concentrates. Of the 25 leading mines producing gold in 1972, 15 were copper based ores and two were lead-zinc ores. In the absence of cyanidation, smelting would continue as a source of gold. However, since the gold produced by smelting is largely a by-product, the gold production depends almost entirely on the production of the base metals.

The use of malonitrile for chemical leaching of gold has been studied by the Bureau of Mines[2/] but is not an alternative for cyanidation because of lower efficiency and higher costs.

In conclusion, currently there are no alternatives to the use of cyanides in the production of gold, if the approximate level of production is to be continued.

Cyanides are used in flotation as depressants, thereby inhibiting the flotation of certain minerals while recovering other mineral values. As shown in Table 43, cyanides strongly depress the iron and zinc sulfides while cyanides moderately depress copper sulfides.

In copper ores and lead ores cyanides might be replaced by reducing agents or in some cases no depressants might be used for flotation recovery. Adverse effects would probably be monetary penalties paid to smelters for increased sulfur loads in the form of iron sulfides and increased transportation costs for hauling worthless gangue minerals. Without the use of cyanide in the lead-zinc-copper separation, some zinc would be lost to the copper and lead concentrates, and smelting penalties would be assessed for the removal of zinc. The definite possibility also exists that the concentrates may not be marketable if they contain the impurities which the cyanides depress.

The literature indicates that cyanides are the most prevalent depressant used for the flotation recovery of molybdenum from copper-molybdenum ores.[3/] Reference is also made to the use of roasting, steaming, sodium sulfide, potassium dichromate, and Noke's Reagent (P_2S_5 or As_2S_5 plus NaOH) as methods of depressing copper while floating molybdenum. Alternatively, dextrin may be used to depress molybdenum while floating copper; however, this method of separation is usually much less efficient than depressing the copper sulfides. In the case of roasting, the surfaces of the copper grains are oxidized and become nonfloatable while the molydenite remains floatable.[3/] Roasting may be an expensive method of copper depression and SO_2 is a by-product. Steaming is an energy intensive operation. Potassium dichromate is a powerful oxidant which oxidizes the collector from the copper sulfide surface. Noke's Reagent is a powerful depressant, but H_2S fumes can be evolved if care is not taken in its preparation.

In the use of cyanide to depress zinc, no current viable alternatives seem available. In the absence of cyanide used as a depressant for zinc, zinc recovery would surely decline. Smelting of lead concentrates containing zinc results in loss of zinc to the slag.[4/] The use of cyanide to depress zinc would be included in most of the processes recovering mineral values from copper-lead-zinc ore, copper-zinc iron-sulfide ore, lead-zinc ore and lead-zinc-silver ore.

Fluorspar ore flotation may have no substitute for cyanide. The lowest marketable grade of fluorspar must contain less than 0.3% sulfide sulfur, and the highest grade must contain less than 0.1% sulfide sulfur.

In conclusion, the substitution of other depressants for cyanides to depress copper and iron sulfides would probably increase the sulfur load at copper smelters and may lessen the recovery of molybdenum. The elimination of cyanides to depress zinc would surely lower the recovery of zinc and likely result in smelter penalties.

Metal Heat Treatment

Liquid Carburizing - Alternatives to liquid carburizing and some disadvantages of each alternative follow in Table 72.

Table 72. ALTERNATIVES TO LIQUID CARBURIZING

Alternative	Disadvantages of Alternative
1. Gas carburizing using natural gas, propane and derivatives	a. Toxic CO produced
	b. Generally not as fast
	c. Less maximum case depth
	d. Flammable, explosive atmosphere
	e. Furnaces generally more expensive
	f. Gas metering equipment necessary
	g. Equipment less versatile
	h. Requires more skilled operation
2. Solid carburizing using coke or charcoal	a. Much harder to control case depth
	b. Much slower
	c. Cannot be directly quenched
	d. Equipment less versatile
	e. Less efficient heat utilization
3. Noncyanide salt baths	a. Requires more skilled operation[1/]
	b. Not as versatile[1/]
	c. The salt is presently more expensive

In summary, gas carburizing and use of noncyanide salt baths for liquid carburizing will likely continue to displace the use of cyanide for case hardening. This is especially true for smaller heat treating shops. Gas carburizing currently is more widely practiced than liquid carburizing.

Liquid Nitriding - A direct alternative to liquid nitriding is gas nitriding. Gas nitriding uses ammonia and dissociated ammonia as the gaseous atmosphere.

The disadvantages of gas nitriding are essentially the same as for gas carburizing except toxic carbon monoxide is not produced. However, ammonia is discomforting and must not be allowed to permeate the working environment.

Two additional disadvantages with gas nitriding are firstly, that it is not applicable to case hardening of plain carbon steel.[2/] Secondly, the case produced by gas nitriding is more brittle than that produced by liquid nitriding.[3/]

However, gas nitriding will likely continue to replace liquid nitriding in the future. Currently, gas nitriding is more prevalent than liquid nitriding.

Liquid Carbonitriding - The alternative to liquid carbonitriding is a combination of gas carburizing and gas nitriding, commonly called gas cyaniding, dry cyaniding or nicarbing.

The same general disadvantages apply to gas carbonitriding as to gas carburizing and gas nitriding. Again, gas carbonitriding will most likely continue to replace liquid carbonitriding.

Less Specific Alternatives - Other methods of case hardening could also replace the use of cyanides in specific instances. These methods include:

Induction hardening
Flame hardening
Surface alloying
Siliconizing

These processes are currently in use to varying degrees.

Photographic Processing Chemicals

A substitute for ferro-ferricyanide photographic bleach is the so-called "blix" solution based on an EDTA-Na-Fe redox system.[1/] The term "blix" is short for bleach-and-fix and refers to a process in which the bleaching and fixing steps are combined. In the normal bleach bath (ferro-ferricyanide-bromide) the silver present in the film is oxidized and converted to silver bromide. A subsequent fixing bath (hypo) dissolves the silver bromide so that it may be washed from the film and the normal sequence of operations is bleach, rinse, fix, and rinse.

A bleach-fixing bath (blix) can accomplish the same results in one step followed by a rinse. In general, the blix bath consists of a ferri-EDTA complex and hypo. The former component oxidizes silver and is reduced to a ferro-EDTA complex. As this happens the hypo complexes the silver ion so that it can be washed from the film. The ferro-EDTA complex may be reacted with dissolved oxygen provided by aeration and reoxidized to the original ferri complex. Silver may be removed by iron displacement, ion exchange methods, or electrolytically to rejuvenate the bath.

The blix solution is kinetically slower than a conventional ferro-ferricyanide bleach solution. A catalyst such as a polyglycol, a stabilizer such as sulfite, and pH control are essential in satisfactory blix bath operation.

The advantages of a blix bath are a shorter overall processing times due to elimination of fix and rinse steps, elimination of ferricyanide, and avoidance of potential iron blue precipitation in the bleach bath.

Disadvantages of the blix bath are that the system requires closer control during operation than conventional ferricyanide bleach baths, that additional chemical components must be present for an active yet stable bath, and that silver metal is not as easily recovered by electrolysis due to the ferri-EDTA complex. Further, the usual film hardening agents such as formalin or potassium alum cannot be used in a blix bath because of conflicting pH requirements.

Research on blix baths has been an active field of investigation for the past 30 years and remains so today. According to Roosen and his co-workers, no known blix bath has the simultaneous advantages of good activity, stability, and hardening properties without some unwanted side effects.[1]

Equipment changes are minimal in converting from a conventional bleach-rinse-fix-rinse operation to a two-step blix operation. The equipment in many film processing laboratories consists of a combination of hand-made developing and rinsing tanks and/or those modified from commercial units to suit a particular need. Conversion from one system to another is relatively simple and inexpensive and there appears to be no overriding economic factors to hinder the conversion. There appears to be a definite economic advantage in converting to the blix system since the overall processing time is shorter with no loss in film quality.

The ferri-EDTA-hypo blix solution has not yet completely replaced the ferricyanide bleach bath but is gaining prominence. Conventional color print processes were the first to use blix baths with color negative processes following. Color reversal processes and motion picture film developing primarily still depend largely on conventional ferricyanide bleach baths. Industry sources anticipate continued growth in blix bath usage over the next 10 years. The ecological implications of large-scale (several millions of pounds) usage of ferri-EDTA complex are not clear.[2] On the other hand, ferro- and ferricyanide regeneration and effluent treatment is well known and poses no insurmountable problems. According to Cooley, ferricyanide bleach bath will remain in wide use in the foreseeable future.[3]

Anti-Caking Agents

There are no recommended alternate chemicals as substitutes for iron blue or sodium ferrocyanide as anti-caking agents in de-icers for highway use. According to the Salt Institute, Alexandria, Virginia, iron blue or ferrocyanide have been used for this purpose since 1921 and no adverse effects related to these chemicals have been noted.[1] Hence, there is no good reason to make a change.

Common table salt does contain anti-caking agents such as ferric ammonium citrate and sodium ferrocyanide. Ferrocyanide has been approved by the FDA for use as an anti-caking agent at 500 ppm.[2]

Agricultural and Pest Control Chemicals

Hydrogen cyanide and calcium cyanide have all but disappeared as agricultural and pest control chemicals. It is estimated that perhaps 50,000 to 60,000 lb of liquid hydrogen cyanide are dispersed annually for fumigation purposes. This amount could increase significantly in the future if grain surpluses return, for then vast amounts of grain in storage bins and elevators across the country would require fumigation.

Present solid and liquid fumigants work well and no significant change in their usage pattern is indicated at present. A slight increase of usage in the future is indicated if food production continues to increase. The development of new fumigants is not anticipated in the near future unless some of the present ones are shown to be detrimental for one reason or another. The current market appears to have stabilized.

There is quite a bit of activity in the pest control sector, principally for rodenticides.[1] Sorex, Ltd. (London), now markets Neosorexa in Britian and Europe. The active agent is difenacoum and kills rodents which are resistant to other anticoagulants such as Warfarin. Sorex intends to market Neosorexa in the U.S. through ICI United States of Wilmington, Delaware. Sorexa CR which combines Warfarin with calciferol, vitamin D-2, is an alternate rodenticide.

Rohm and Haas has recently developed Vacor, a new rodenticide, based on a derivative of p-nitrophenyl urea. It is marketed as a 2% grain-bait, and a bentonite tracking powder for mice is planned.

Other new rodenticides based on Vitamins D-2 or D-3 in conjunction with warfarin are being tested for both rats and mice. Sorex Limited (London) and Bell Laboratories, Inc., of Madison, Wisconsin, are the developers.

Finally, chemosterilization has potential as a pest control technique, but no product has yet emerged. Research and development in steroids and chloroaliphatic diols are continuing.

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CHAPTER X

MATERIAL BALANCE AND ENERGY CONSUMPTION

In this section, the material and energy requirements for the production of inorganic cyanides will be discussed. A material balance of the industrial uses of cyanides is presented in detail. Also included is a discussion on the waste produced in the manufacture and use of inorganic cyanide. A final point will be the exposure of man and the environment to cyanides.

RAW MATERIALS

Below are summarized the calculated raw material requirements for various inorganic cyanides produced domestically in 1975 except where noted.

1. Hydrogen cyanide produced as a by-product of acrylonitrile production in the SOHIO process.

1974 acrylonitrile production[1]	1.36×10^9 lb
hydrogen cyanide at 0.15 lb/lb acrylonitrile	200×10^6 lb
raw materials required at 85% yield[2]	
propylene	1.8×10^9 lb
ammonia	450×10^6 lb

2. Hydrogen cyanide produced by the Andrussow process.

hydrogen cyanide (MRI estimate)	275×10^6 lb
raw materials required[3]	
methane	165×10^6 lb
ammonia	170×10^6 lb

3. Sodium cyanide produced by neutralization of hydrocyanic acid.

1975 sodium cyanide (MRI estimate)	56.5×10^6 lb
raw materials required at 100% yield	
hydrogen cyanide	31×10^6 lb
sodium hydroxide	47×10^6 lb

4. Iron blue production.

1975 iron blue (estimate)	8.0×10^6 lb
raw material[3/]	
ferrous sulfate	8.8×10^6 lb
sodium ferrocyanide	1.4×10^6 lb
sulfuric acid	2.6×10^6 lb
ammonium sulfate	2.4×10^6 lb
sodium chlorate	1.0×10^6 lb

5. Sodium ferrocyanide production.

sodium ferrocyanide, decahydrate (estimate)	2.5×10^6 lb
raw materials at 100% yield	
calcium cyanide	1.3×10^6 lb
ferrous sulfate	0.8×10^6 lb
sodium carbonate	1.1×10^6 lb

6. Sodium ferricyanide production by chlorine oxidation of sodium ferrocyanide.

sodium ferricyanide, monohydrate (estimate)	0.4×10^6 lb
raw materials at 100% yield	
sodium ferrocyanide, decahydrate	0.6×10^6 lb
chlorine	0.05×10^6 lb

ENERGY CONSUMPTION FOR PRODUCTION

Listed below are the energy consumptions for the production of inorganic cyanides, differentiated by process where applicable. The figures listed are average and specific process energy consumption may be higher or lower depending on the reaction conditions used. This would be particularly true in the case in acrylonitrile processes where the reaction temperatures and pressures may be different for different catalysts.

1. By-product hydrogen cyanide from acrylonitrile production:[4/]

	Per 1,000 lb acrylonitrile*
Electricity	180 kwh
Steam (at 60 psig)	100 lb
Fuel (other than for steam)	None

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* Approximately 150 lb of hydrogen cyanide would be produced.

2. Hydrogen cyanide by the Andrussow process:

	Per 1,000 lb hydrogen cyanide
Electricity	420 kwh
Steam and fuel	None

3. Sodium cyanide and potassium cyanide by neutralization:

	Per 1,000 lb sodium or potassium cyanide
Electricity	15 kwh
Steam	1,650 lb
Fuel (other than for steam)	None

WASTE MATERIAL PRODUCT

Waste produced in the manufacture of inorganic cyanides in most cases is minimal with the exceptions of iron blue and ferrocyanide production. Waste production can be in gaseous, liquid or solid form depending on the cyanide produced.

By-Product Hydrogen Cyanide

Hydrogen cyanide is produced domestically as a by-product of acrylonitrile production by the SOHIO process. The reactants are all gaseous and the process is at high temperature. Wastes produced are:

Solid waste: Insignificant amounts of silica catalyst result, presenting no disposal problems.[4/]

Liquid waste: Liquid wastes in acrylonitrile production are the most significant. Water used for absorption of the products, later distilled off, may contain several organic compounds as nitriles and cyanides including hydrogen cyanide which necessitates treatment. Liquid wastes from these processes can be adequately treated by most of the methods discussed in Chapter VIII.

Gaseous wastes: Several gaseous wastes are produced which may contain hydrogen cyanide as an impurity. These gases are usually vented to the air through a flare. The heat value of the gases is too low for use in firing boilers, if the hydrogen cyanide is removed. The gases may be suitable for combustion as boiler fuel, if the HCN is not recovered.

Primary Hydrogen Cyanide

Hydrogen cyanide is produced directly in the Andrussow process. Like the SOHIO acrylonitrile process, the reaction is between gaseous reactants. Waste materials include:

Solid waste: Essentially none, since the catalyst is of the platinum group metals and is recovered.

Liquid wastes: Liquid wastes result from water used in the process. Cyanide contaminants are in the form of hydrogen cyanide and salts including cyanide in association with ammonia. These wastes would lend well to the treatment techniques presented in Chapter VIII.

Gaseous wastes: Wastes in the gas form are essentially the same as those from acrylonitrile production.

Sodium Cyanide by Neutralization

In the production of sodium cyanide, hydrogen cyanide (hydrocyanic acid) is neutralized with caustic soda in aqueous solutions. Waste materials include:

Solid and gaseous: Essentially no solid or gaseous wastes are produced since a balance between caustic and hydrocyanic acid is required.

Liquid wastes: Liquid wastes from sodium cyanide production are water solutions containing sodium cyanide. Treatment is necessary before discharge. These water wastes are ideally suited for alkaline chlorination.

Iron Blue

Production of iron blue pigments produces much waste material, see Figure 12, Chapter VI.

Solid waste: Sulfuric acid is used in the production of iron blue, which is neutralized with hydrated lime. This not only precipitates as calcium sulfate, but also causes complex iron cyanides and hydrated iron oxides to precipitate. The result is a large quantity of solid residue which may contain free cyanide impurities.

The literature indicates that this solid waste is disposed in landfill, both on and off the production site.[3]

Liquid waste: Water is used for washing the iron blue pigments and for carrying the excess sulfuric acid and iron salts in iron blue production. Ammonium salts are contained in the water. Solids are precipitated as above and removed from solution. The water likely still contains cyanide impurities which should be treated before discharge.

Gaseous waste: Almost no gaseous wastes are produced in iron blue manufacture.

Sodium Ferrocyanide

Manufacture of sodium ferrocyanide produces much solid waste and potentially toxic aqueous waste.

Solid waste: In the production of sodium ferrocyanide, solid wastes include calcium sulfates, carbonates and hydroxides as well as complex iron cyanides and hydrated oxides. Residual process water in the solid wastes may also contain dissolved cyanide salts.

Liquid waste: Liquid wastes include the water used in the reaction and water for washing. The water probably contains sodium and calcium cyanides not reacted and not precipitated. Part of the water is recycled to the production stream.

Gaseous waste: Essentially no gaseous waste results from sodium ferrocyanide production.

Sodium Ferricyanide

Sodium ferricyanide is manufactured by chlorine oxidation of sodium ferrocyanide. Wastes are:

Solid waste: Essentially no solid waste is produced.

Liquid waste: Liquid waste consists of process and wash water. This water could contain small amounts of the ferricyanides and ferrocyanides as well as residual chlorine.

Gaseous waste: Waste material in the gaseous form consists mainly of chlorine gas which can be recycled to the process.

In conclusion, two questions arise:

1. How effective is a flare in destroying residual HCN in vent gases from acrylonitrile and hydrogen cyanide production?

2. What is the fate of ferrocyanide, ferricyanide, iron blue, and other complex iron cyanides in essentially anaerobic landfill conditions?

MATERIAL BALANCE OF CYANIDE BY INDUSTRIAL SECTOR

Figure 28 presents a detailed material balance for the production of HCN and other cyanides as NaCN equivalent. Of the estimated 375 million pounds of HCN produced in 1975, 41.2 million pounds of HCN or 75 million pounds as NaCN equivalent entered the inorganic industrial sector. Net imports of various cyanides accounted for 15 million pounds of NaCN equivalent.

The merchant sales sector accounts for approximately 53 million pounds of NaCN and 27 million pounds of NaCN equivalent as ferro- and ferricyanides, iron blue, calcium cyanide, and heavy metal cyanides distributed over seven categories. Table 73 indicates the estimated contribution of each sector as NaCN or NaCN equivalent.

Figure 28 also presents disposal methods with prominent choices underlined for each sector. The highly toxic cyanide ion is primarily treated by alkaline chlorination. Other less toxic cyanides such as ferrocyanide and iron blue are either disposed of in municipal sewers, landfilled, or occur in runoff water.

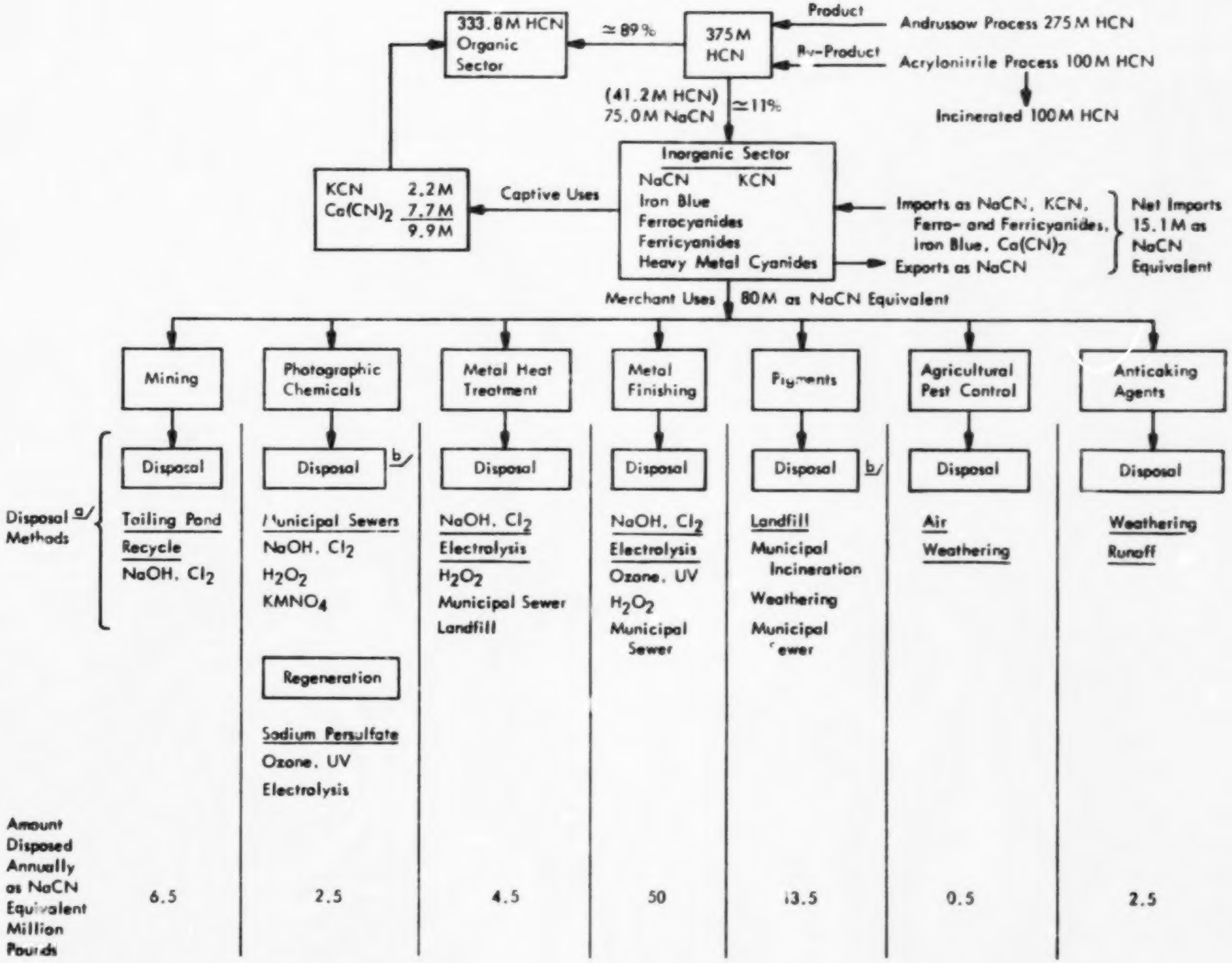
Note that regeneration is prominent only in the photographic processing chemicals sector. The economics are favorable but it is estimated that perhaps only 15 to 20% of the ferrocyanide is now being regenerated.

EXPOSURE TO MAN AND THE ENVIRONMENT

The inorganic cyanides are generally end-products for industrial use. These cyanides, with the exception of iron blue pigments and photographic chemicals, do not reach the consumer market as cyanides. Each industrial sector is discussed to present the magnitude of exposure.

Electroplating

Approximately 50 million pounds of NaCN equivalent are consumed annually in electroplating, principally as sodium cyanide. It is estimated that one-half of the cyanide consumption is due to oxidation by electrolysis in the plating bath.[5]


333.8 M HCN Organic Sector
≃ 89%
375 M HCN
Product
Andrussow Process 275 M HCN
By-Product
Acrylonitrile Process 100 M HCN
Incinerated 100 M HCN
(41.2 M HCN) 75.0 M NaCN
≃ 11%
Inorganic Sector
NaCN KCN
Iron Blue
Ferrocyanides
Ferricyanides
Heavy Metal Cyanides
KCN 2.2 M
Ca(CN)2 7.7 M
9.9 M
Captive Uses
Imports as NaCN, KCN, Ferro- and Ferricyanides, Iron Blue, Ca(CN)2
Exports as NaCN
Net Imports 15.1 M as NaCN Equivalent
Merchant Uses
80 M as NaCN Equivalent
Mining
Photographic Chemicals
Metal Heat Treatment
Metal Finishing
Pigments
Agricultural Pest Control
Anticaking Agents
Disposal
Disposal b/
Regeneration
Disposal a/ Methods
Tailing Pond
Recycle
NaOH, Cl2
Municipal Sewers
NaOH, Cl2
H2O2
KMNO4
Sodium Persulfate
Ozone, UV
Electrolysis
NaOH, Cl2
Electrolysis
H2O2
Municipal Sewer
Landfill
NaOH, Cl2
Electrolysis
Ozone, UV
H2O2
Municipal Sewer
Landfill
Municipal Incineration
Weathering
Municipal Sewer
Air
Weathering
Weathering
Runoff
Amount Disposed Annually as NaCN Equivalent Million Pounds
6.5
2.5
4.5
50
13.5
0.5
2.5

a/ Major methods of disposal are underlined.

b/ Including disposal methods for consumer products.

Figure 28. Material balance for the production of HCN and other cyanides as NaCN equivalent (million lb)

Table 73. NaCN and NaCN EQUIVALENT BY INDUSTRIAL SECTOR

Industrial sector	NaCN (million lb)	NaCN equivalent (million lb)	Total
Metal finishing			50
Plating, stripping	43		
Heavy metal cyanides		7	
Pigment			13.5
Iron blue		13.5	
Mining - flotation			6.5
and extraction	5.3	1.2	
Metal heat treatment	4.4	0.2	4.6
Photographic chemicals		2.5	2.5
Anti-caking agents		2.5	2.5
Agriculture and pest control		0.5	0.5
Total	53	27	80

Source: MRI estimate

Nearly 25 million pounds of the cyanide consumed is dragged out of the plating bath into the rinse waters. Cyanides in the rinse water require treatment prior to discharge. Of very minor consequence are spills and deliberate dumping of concentrated plating solutions. Provisions are usually made in those events to add the spills to the rinse waters for treatment.

It has been estimated that nearly all of the cyanide released is treated by some means, usually alkaline chlorination. It is possible that some small plating shops in large cities may not treat wastes and may discharge directly to municipal sewer systems. This figure is estimated at < 1% of total cyanide consumption in metal finishing.

The exposure of cyanides from electroplating is minimal both to man and the environment due to general treatment of the wastes.

Pigments

Approximately 13.5 million pounds (NaCN equivalent) of iron blue pigments are consumed annually in the U.S. These pigments are components in printing inks, carbon paper, typewriter ribbons and, to a much smaller extent, paints.

Nearly all of these 13.5 million pounds of iron blue pigments are exposed to man and the environment. This exposure is extremely widespread and any immediate adverse impacts more likely would be due to solid waste disposal of the medium carrying the pigments than due to the pigments. Also the toxicity of the iron blue pigments is extremely low.

Not known are the long-term effects of iron blue pigments exposed to the environment, particularly those disposed to landfills. The greatest part of these pigments are disposed of in this manner.

Mining

The mining industry currently consumes approximately 6.5 million pounds as NaCN equivalent annually. The cyanides are sodium cyanide, sodium ferrocyanide and calcium cyanide. All of the total annual consumption of these cyanides enter the environment, generally by way of tailing ponds. The consequences of this exposure is minimized with management of the tailing ponds.

Management of the tailing ponds include:

- Vegetation of the dam to prevent failure;
- Control of runoff water;
- Storage of water seepage through the dam in retention ponds;
- Adequate size for lengthy retention times;
- Recycle of water to the mill; and
- Dams constructed on relatively impermeable soil.

The cyanides are also subjected to natural degradation by sunlight, air and biological processes. Free cyanide may become attached to mineral and carbonaceous solids present and settle out. In more arid climates evaporation will consume all excess water with no discharge from the tailing pond.

Preliminary data soon to be published by Calspan Corporation indicate that cyanide in tailing pond effluents from lead and zinc milling operations is less than 0.01 mg/liter. Effluents from copper and copper-molybdenum should be comparable and in many cases essentially zero, as these operations are predominantly located in arid climates where evaporation from tailing ponds consumes all excess water.

There has been no reported leakage from gold and silver plant tailing ponds.[6] However, one major gold producer is reported not to use tailing ponds, but direct discharge of excess mill water. No data were found to indicate the amount of cyanide lost to the environment from this producer.

In conclusion, it is estimated that less than 10% of the cyanides used in mining escaped to the environment uncontrolled. However, the cyanide contained in tailing ponds may be a potential hazard, especially to wildlife.

Heat Treating

In the metal heat treating industry, 4.5 million pounds of sodium cyanide are consumed annually. This consumption results from the following: (a) drag-out to the quenching medium; (b) high temperature air oxidation at the surface of the bath; and (c) reaction to produce the hard case on the parts.

Of environmental concern is the drag-out to the quenching medium. Nearly all of the cyanides are treated prior to disposal much the same as in electroplating. In fact many of the captive heat treaters are operated in conjunction with electroplating operations. Treated waters in most cases are discharged to municipal sewers.

In summary, very little exposure to man and the environment occurs due to treatment of cyanides from the metal heat treating industry.

Photographic Chemicals

Approximately 2.5 million pounds of cyanides as NaCN equivalent are used in the photography industry annually, principally as ferricyanides and ferrocyanides.

All of the 2.5 million pounds consumed annually are lost from the photographic processes. Most of these cyanides are discharged to municipal sewer systems by continuous discharge of rinse water. The rinse waters contain low concentrations of these cyanides (i.e., $<$ 1 ppm concentration). Only very occasionally would concentrated baths be dumped and then probably with large quantities of water as diluent.

The ferrocyanide and ferricyanide subjected to primary treatment in municipal sewage plants would likely be separated with the solid matter. The cyanides could be absorbed on the organic constituents or complexed with metallic compounds.

The sewage sludge may be disposed by spreading on land, both agricultural and nonagricultural. Consequently, the ferro- and ferricyanides from photographic processes may be not only exposed to man and the environment, but also introduced to the food chain.

Anti-Caking Ingredient in De-Icing Salts

Sodium ferrocyanide and iron blue are used as an anti-caking ingredient in salt used for thawing ice, mainly on roads. Approximately 2.5 million pounds as NaCN equivalent are used in this manner yearly.

All of this 2.5 million pounds is exposed to the environment and subject to runoff from the roads. Through storm sewers the ferrocyanide will ultimately reach waterways. There the environmental effects may be the greatest, as ferrocyanide can decompose in sunlight to cyanide which is toxic. The ferrocyanides themselves are low in toxicity.

Agricultural and Pest Control

No hard data are to be found on the consumption of inorganic cyanides used for agricultural pest control of rodents and predators. The estimate is perhaps 0.5 million pounds each year. Hydrogen cyanide is still used in small amounts in fumigation of grain and seed in storage. Sodium and calcium cyanide are used against rodents and sodium cyanide may be used for predator control.

All of the cyanides used for pest control enter the environment. Hydrogen cyanide used for control of rodents would likely be used in remote areas such as garbage dumps and grain storage areas. The use of sodium cyanide for control of predators, namely coyotes, would be limited to sparsely populated rangelands.

Tables 74 through 78 present a summary of the estimated amounts of inorganic cyanides that entered the environment in 1965, 1970, 1975, 1980, and 1985. The tables are self-explanatory and indicate release and exposure to the environment of cyanide (as ferrocyanide and iron blue) for the years indicated. Essentially all the ferrocyanide from de-icers is released in runoff water, and under the action of sunlight cyanide ion may be released and subsequently oxidized to cyanate, which is much less toxic than cyanide (by a factor of ~ 1,000). Iron blue enters the local treatment system as solid waste and approximately 10% is incinerated and decomposed. The remaining 90% becomes part of a landfill.

The decomposition kinetics of ferrocyanide due to normal weathering in ditches by the highway and iron blue in landfill (presumably anaerobic decomposition) are unknown. Tables 74 through 78 assume a relatively slow decomposition rate of 5%/year.

Figure 29 presents the estimated total amount of ferrocyanide and iron blue as environmental burden over the years 1950 to 1985 and was developed from data similar to those presented in Tables 74 through 78. Five sets of exposure data are presented assuming degradation rates of 5, 10, 20, 50 and 100%/year. At a degradation rate of 100%/year, the amount of cyanide burden becomes approximately one half the annual usage rate or about 8 million pounds in 1975. At a degradation rate of 50%/year, the amount of cyanide burden becomes approximately 1.5 times the annual usage rate or 24 million pounds in 1975.

Table 74. ESTIMATED AMOUNT OF CYANIDE AS NaCN EQUIVALENT IN USE AND EXPOSED TO THE ENVIRONMENT AND MAN, 1965-1985
(million lb)

Industrial sector	Annual consumption	Inventory	Reservoir in use	Release and exposure to local treatment plant	Release and exposure to environment in 1965	Amount of cyanide in environment by sector as ferro- and ferricyanides			
						1970	1975	1980	1985
Metal finishing	44.0	3.7	220.0	11.0	0	0	0	0	0
Pigment	12.3	1.0	12.3	12.3	11.1	8.3	5.5	2.8	0
Mining	5.0	0.4	0.5	0	1.5	0	0	0	0
Metal heat treatment	4.3	0.4	21.5	2.2	0	0	0	0	0
Photographic processing	4.2	0.4	4.2	4.2	3.8	2.8	1.9	1.0	0
Anti-caking agents	2.5	1.2	1.2	0	2.5	1.9	1.2	0.6	0
Agriculture and pest control	2.0	0.2	2.0	0	2.0	0	0	0	0
Total	74.3	7.3	261.7	29.7	20.9	13.0	8.6	4.4	0

Table 75. ESTIMATED AMOUNT OF CYANIDE AS NaCN EQUIVALENT IN USE AND EXPOSED TO THE ENVIRONMENT AND MAN, 1970-1985
(million lb)

Industrial sector	Annual consumption	Inventory	Reservoir in use	Release and exposure to local treatment plant	Release and exposure to environment in 1970	Amount of cyanide in environment by sector as ferro- and ferricyanides		
						1975	1980	1985
Metal finishing	55.0	4.6	275.0	14.0	0	0	0	0
Pigment	12.9	1.1	12.9	12.9	11.6	8.7	5.8	2.9
Mining	6.6	0.6	0.7	0	1.6	0	0	0
Metal heat treatment	4.9	0.4	24.5	2.4	0	0	0	0
Photographic processing	5.0	0.4	5.0	5.0	4.5	3.4	2.2	1.1
Anti-caking agents	2.5	1.2	1.2	0	2.5	1.9	1.2	0.6
Agriculture and pest control	1.0	0.1	1.0	0	1.0	0	0	0
Total	87.9	8.4	320.3	34.3	21.2	14.0	9.2	4.6

Table 76. ESTIMATED AMOUNT OF CYANIDE AS NaCN EQUIVALENT IN USE AND EXPOSED TO THE ENVIRONMENT AND MAN, 1975-1985 (million lb)

Industrial sector	Annual consumption	Inventory	Reservoir in use	Release and exposure to local treatment plant	Release and exposure to environment in 1975	Amount of cyanide in environment by sector as ferro- and ferricyanides	
						1980	1985
Metal finishing	50.0	4.2	250.0	0.5	0	0	0
Pigment	13.5	1.1	13.5	13.5	12.1	9.1	6.0
Mining	6.5	0.5	0.5	0	1.5	0	0
Metal heat treatment	4.5	0.4	22.5	< 0.1	0	0	0
Photographic processing	2.5	0.2	2.5	2.5	2.2	1.6	1.1
Anti-caking agents	2.5	1.2	1.2	0	2.5	1.9	1.2
Agriculture and pest control	0.5	< 0.1	0.5	0	0.5	0	0
Total	80.0	7.7	290.7	16.6	18.8	12.6	8.3

Table 77. ESTIMATED AMOUNT OF CYANIDE AS NaCN EQUIVALENT IN USE AND EXPOSED TO THE ENVIRONMENT AND MAN, 1980-1985
(million lb)

Industrial sector	Annual consumption	Inventory	Reservoir in use	Release and exposure to local treatment plant	Release and exposure to environment in 1980	Amount of cyanide in environment by sector as ferro- and ferricyanides
						1985
Metal finishing	43.8	3.6	219.0	0.4	0	0
Pigment	16.2	1.4	16.2	16.2	14.6	11.0
Mining	6.5	0.5	0.6	0	1.5	0
Metal heat treatment	3.4	0.3	17.0	< 0.1	0	0
Photographic processing	1.2	0.1	1.2	1.2	1.1	0.8
Anti-caking agents	2.5	1.2	1.2	0	2.5	1.9
Agriculture and pest control	0.1	< 0.1	0.1	0	0.1	0
Total	73.7	7.2	255.3	17.9	19.8	13.7

Table 78. ESTIMATED AMOUNT OF CYANIDE AS NaCN EQUIVALENT IN USE AND EXPOSED TO THE ENVIRONMENT AND MAN IN 1985
(million lb)

Industrial sector	Annual consumption	Inventory	Reservoir in use	Release and exposure to local treatment plant	Amount of cyanide in environment by sector as ferro- and ferricyanides 1985
Metal finishing	37.5	3.1	188.0	0.4	0
Pigment	18.4	1.5	18.4	18.4	16.6
Mining	6.5	0.5	0.6	1.5	1.5
Metal heat treatment	2.2	0.2	11.0	< 0.1	0
Photographic processing	1.0	0.1	1.0	1.0	0.9
Anti-caking agents	2.5	1.2	1.2	2.5	2.5
Agriculture and pest control	0	0	0	0	0
Total	68.1	6.6	220.2	23.9	21.5

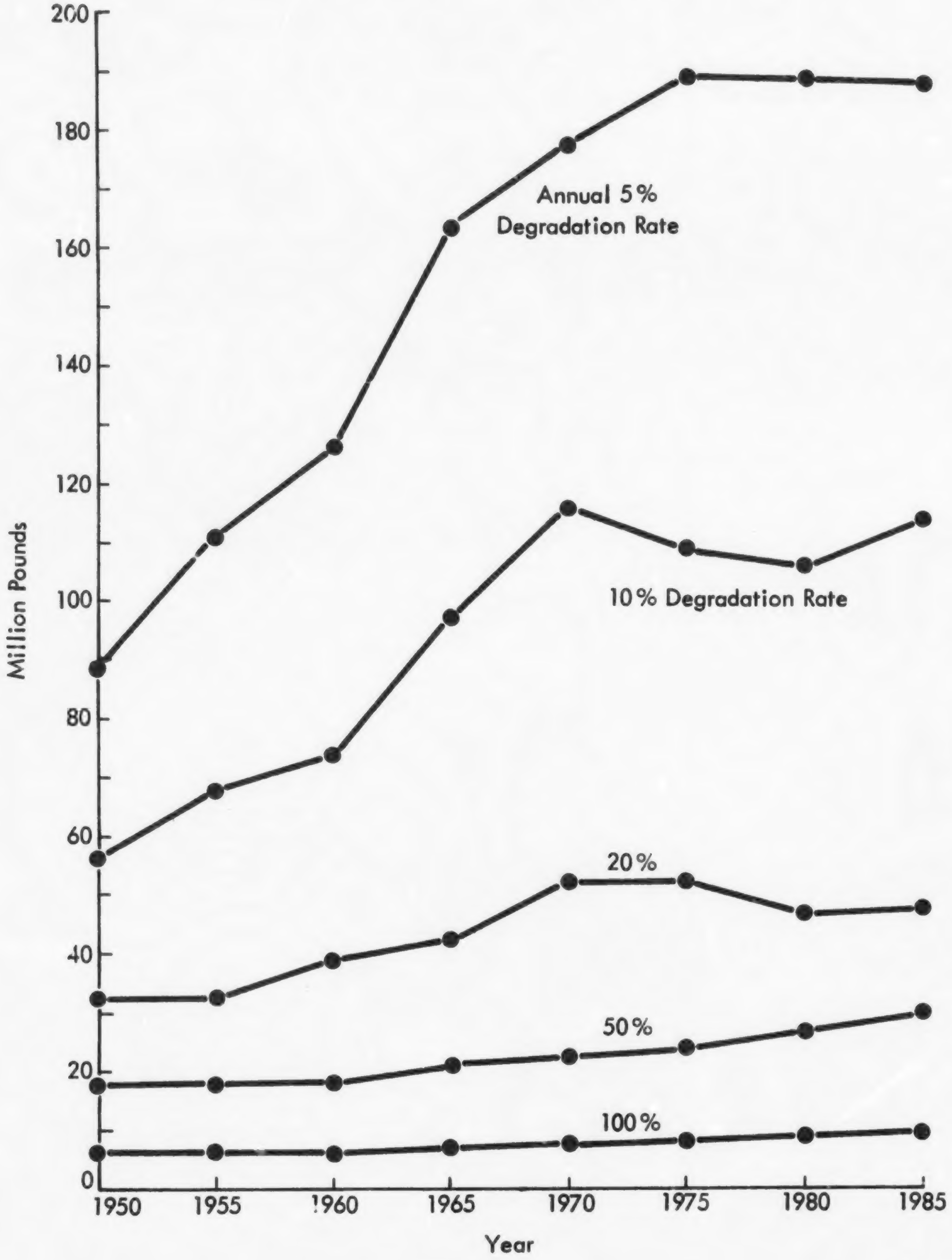


Figure 29. Estimated total amount of ferrocyanide and iron blue as environmental burden, 1950-1985

Four important points are to be made in connection with estimating future ferrocyanide and iron blue burden on the environment:

- Degradation rates of ferrocyanide in roadside ditches exposed to normal sunlight and weathering conditions require quantification.
- Degradation rates of iron blue under anaerobic landfill conditions require quantification.
- Cyanide burden as ferrocyanide from de-icers depends on usage rates of the de-icers and the amount added per ton of salt.
- Cyanide burden as iron blue depends on the extent to which iron blue remains an important pigment.

Quantitative information on residual ferrocyanide and iron blue environmental burden is totally lacking. Figure 29 is best interpreted as a range of possible environmental burdens over the last 25 years with a projection of declining total cyanide usage to 1985. A more meaningful interpretation must await quantification of degradation rates of ferrocyanide and iron blue under various environmental conditions.

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APPENDIX A

THERMALLY GENERATED CYANIDE SOURCES

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Thermally generated cyanides may be taken as cyanides resulting from high temperature reaction of carbon and nitrogen compounds in a reducing atmosphere. These conditions are met most favorably in coking operations, blast furnace production of iron and ferroalloys, and operations producing ferroalloys other than by blast furnaces. Each of these operations is discussed briefly below, with estimated quantities of cyanides generated where data were available.

COKE PRODUCTION

In the production of coke, coal is externally heated at about 1100°C, in the absence of air (pyrolysis) for approximately 18 hr. In the process, materials volatile at 1100°C are driven from the coal.

Two types of ovens are used in the U.S. to make coke: (a) by-product ovens and (b) beehive ovens. The main distinction between the two is that with by-product ovens the volatile matter can be collected and processed for recovery of the different chemical constituents. The volatile gases are not collected, but allowed to escape to the atmosphere in coke production from beehive ovens. Beehive oven operation is minor domestically, with only 1% of total coke production in 1972.[1] Table A-1 details the number of each type of oven in operation in 1974.

The reactions in the oven producing hydrogen cyanide can probably be attributed to one or more of the following:[2]

$$C_2H_2 + 2NH_3 \longrightarrow 2HCN + 3H_2$$

$$C + NH_3 \longrightarrow HCN + H_2$$

$$CH_4 + NH_3 \longrightarrow HCN + 3H_2$$

$$C_2H_4 + 2NH_3 \longrightarrow 2HCN + 4H_2$$

$$CO + NH_3 \longrightarrow HCN + H_2O$$

The carbon compounds and the ammonia are produced by the breakdown of the coal.

Table A-1. COKE OVENS OPERATED IN THE UNITED STATES AS OF JANUARY 1, 1974[2]

	Number of coke ovens		
Company	Beehive	By-product	Total
Alan Wood Steel Company	-	110	110
Armco Steel Corporation	-	248	248
Bethlehem Steel Corporation	-	2,103	2,103
CF&I Steel Corporation	-	216	216
Crucible, Inc.	-	113	113
Cyclops Corporation			
Empire Detroit Steel Division	-	70	70
Donner-Hanna Coke Corporation[a]	-	151	151
Ford Motor Company	-	205	205
Industrial Products Group			
Woodward Iron Division	-	256	256
Chattanooga Division	-	44	44
Total Industrial Products Group	-	300	300
Inland Steel Company	-	579	579
Interlake, Inc.	-	215	215
International Harvester Company			
Wisconsin Steel Division	-	112	112
Jones & Laughlin Steel Corporation	-	586	586
Kaiser Steel Corporation	-	315	315
Lone Star Steel Corporation	-	78	78
National Steel Corporation			
Granite City Steel Division	-	137	137
Great Lakes Steel Corporation	-	233	233
Weirton Steel Division	-	381	381
Total National Steel	-	751	751
Republic Steel Corporation	-	897	897
Sharon Steel Corporation	-	60	60
Carpentertown Coal and Coke Company	266	-	266
Total Sharon Steel	266	60	326
Shenango, Inc.	-	105	105
United States Pipe and Foundry Company	-	240	240
United States Steel Corporation			
Eastern Steel Division	-	1,962	1,962
Central Steel Division	-	804	804
Western Steel Division	-	252	252
Southern Steel Division	-	489	489
Total U.S. Steel	-	3,507	3,507
Wheeling-Pittsburgh Steel Corporation	-	407	407
Youngstown Sheet and Tube Company	-	549	549
Grand Total	266	11,917	12,183

---

[a] Owned jointly by the Hanna Furnace Corporation and Republic Steel Corporation.

The literature indicates that approximately 0.7 lb of hydrogen cyanide is produced for each ton of coal coked.[3,a] Table A-2 details the coal consumption for coking and the estimated production of hydrogen cyanide for the years 1965, 1970, and 1974.

Table A-2. COAL CONSUMPTION FOR COKING AND CALCULATED HYDROGEN CYANIDE PRODUCTION

Year	Coal consumed for coking (tons)	Reference	Calculated hydrogen cyanide produced from coking (pounds)
1965	95.3×10^6	5	66×10^6
1970	96.5×10^6	6	68×10^6
1974	89.4×10^6[a]	7	63×10^6

---

[a] Estimated coal consumed = $\dfrac{61.5 \times 10^6 \text{ tons coke}}{\dfrac{0.69 \text{ tons coke}}{1 \text{ ton coal}}}$ [b]

[b] Reference 8.

The hydrogen cyanide produced in coking is ultimately lost or consumed by the following: (a) burned as coke oven gas; (b) lost to wastewater;[9] or (c) lost to the air through cooling towers.[9] The amount of hydrogen cyanide burned as a constituent of coke oven gas may approach 80% of the hydrogen cyanide produced in by-product oven coking operations. The coke oven gas is burned not only to heat the coke ovens, but also to preheat air consumed in blast furnaces.

$$\frac{80 \times 10^6 \text{ ft}^3 \text{ oven gas}}{7{,}500 \text{ tons of coal coked}} \times \frac{800 \text{ ft}^3 \text{ HCN}}{1 \times 10^6 \text{ ft}^3 \text{ oven gas}} \times \frac{27 \text{ g HCN}}{22.4 \text{ liters HCN}} \times$$

$$\frac{28.3 \text{ liters}}{1 \text{ ft}^3} \times \frac{1 \text{ lb HCN}}{454 \text{ g HCN}} = 0.64 \text{ lb HCN per ton of coal coked}$$

---

[a] Calculated hydrogen cyanide production from coal coking.[4] Possibly some (~ 10%) of the hydrogen cyanide may have been lost in the process of recovering by-product chemicals (i.e., difference between 0.7 and 0.64 lb HCN per ton of coal coked).

In a recent study by the EPA the water effluents from by-product coke oven installations were analyzed for cyanides.[12] The average water effluent cyanide load was 0.128 lb of hydrogen cyanide per ton of coke produced. This would be equivalent to a total of about 8 million pounds of hydrogen cyanide in water effluents annually for the coking industry, assuming these ovens are typical. Based on the estimated total hydrogen cyanide produced by coking operations in 1974, Table A-2, the hydrogen cyanide in water effluents would constitute about 13% of the total hydrogen cyanide produced by coking.

In the past at least one coke producer, Pittsburgh Coke and Chemical, recovered hydrogen cyanide for sale.[3] No coke producer is now known to recover hydrogen cyanide for sale, probably because of the low value of hydrogen cyanide compared to the difficulties of handling it.

BLAST FURNACE PRODUCTION OF IRON AND FERROALLOYS

Another source of thermally generated cyanides is blast furnace production of pig iron from iron ores. Other metals and ferroalloys can be produced in blast furnaces, but the blast furnace is most associated with iron production. The processes are essentially the same and discussion of pig iron production below can be assumed to apply generally to the other metals and alloys produced in blast furnaces.

In the operation of a blast furnace producing pig iron, iron ore, coke and limestone are charged to the furnace. Hot air is then forced through the charge and the ore is reduced to iron metal by carbon monoxide and hydrogen produced by the reaction of hot air with the coke.

Two essential materials in blast furnaces are coke and hot air. The air can be heated using excess coke oven gas not consumed to heat the coke ovens. For these reasons, most coking operations are located adjacent to the blast furnaces and operated by the same company. Approximately 90% of the coke ovens operated in 1974 were integrated furnace installations.[7]

Some of the reactions involving coke in the blast furnace are:[10]

$$2C + O_2 \longrightarrow 2CO$$

$$C + H_2O \longrightarrow CO + H_2$$

$$FeO + C \longrightarrow Fe + CO$$

Reactions producing iron metal from the ore include:[10]

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

$$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$$

$$FeO + CO \longrightarrow Fe + CO_2$$

$$Fe_2O_3 + 3H_2 \longrightarrow 2Fe + 3H_2O$$

$$Fe_3O_4 + 4H_2 \longrightarrow 3Fe + 4H_2O$$

$$FeO + H_2 \longrightarrow Fe + H_2O$$

The reduction of the iron ore consumes about 50% of the carbon monoxide and hydrogen produced. The remaining 50% can be used for heating in other parts of the steel plant.[10] The blast furnace gases may be burned to supply power for the air compressors supplying the blast furnace or to heat this very same air.[11]

Hydrogen cyanide is produced by the high temperature reaction of coke, nitrogen and water, the nitrogen being introduced in the air or in the coke.

Water effluents from four blast furnaces producing pig iron were sampled and analyzed.[12] The average effluent water load was 0.03 lb of hydrogen cyanide per ton of pig iron produced. The 1972 production of pig iron was nearly 89 million tons.[13] Assuming that the four blast furnace installations sampled represent an average, the total hydrogen cyanide in water effluents from blast furnace operation domestically would be about 3 million pounds in 1972.

No data were found indicating the magnitude of total hydrogen cyanide produced in blast furnace operation.

The final disposal or loss of hydrogen cyanide from blast furnaces may parallel that produced in coke ovens in that the greater portion of hydrogen cyanide is probably burned. Losses of hydrogen cyanide occur to effluent water and to air.

PRODUCTION OF FERROALLOYS OTHER THAN BY BLAST FURNACE

Production of ferroalloys by means other than by blast furnace generally includes production with electric furnaces or exothermic heat processes.[14] The differences are essentially the sources of heat. In many of these processes, coke and air are used as the reducing materials, much the same as with the blast furnaces.

Listed in Table A-3 are ferroalloy producers, locations, products and types of furnaces. Listed in Table A-4 are selected ferroalloy production for the years 1965, 1969, and 1972.

No data were found detailing the amount of hydrogen cyanide resulting from the ferroalloy industry.

Loss of hydrogen cyanide generated in ferroalloy production generally would be to (a) process water and to (b) air. In the electric furnaces operated with an open top, the gases evolved, including hydrogen cyanide, may burn at the surface of the melt. The loss to process water would be in operations where water is used to scrub the gases.

Table A-3. PRODUCERS, LOCATIONS, PRODUCTS, AND FURNACE TYPE FOR FERROALLOY, 1972[15]

Product	Plant location	Product[a]	Type of furnace
Agrico Chemical Company	Pierce, Florida	FeP	Electric
Airco Alloys and Carbide	Calvert City, Kentucky Charleston, South Carolina Mobile, Alabama Niagra Falls, New York	FeCr, FeCrSi, FeMn, FeSi, SiMn	Electric
Alabama Metallurgical Corporation	Selma, Alabama	FeSi	Electric
Bethlehem Steel Corporation	Johnstown, Pennsylvania	FeMn	Blast
Chromium Mining and Smelting Company	Woodstock, Tennessee	FeMn, SiMn, FeCr, FeSi, FeCrSi	Electric
Climax Molybdenum Company	Langeloth, Pennsylvania	FeMo	Aluminothermic
Diamond Shamrock Corporation	Kingwood, West Virginia	FeMn	Electric
FMC Corporation	Pocatello, Idaho	FeP	Electric
Foote Mineral Company	Cambridge, Ohio Graham, West Virginia Keokuk, Iowa Vancoram, Ohio Wenatchee, Washington	FeB, FeCb, FeTi, FeV, FeCr, FeCrSi, FeSi, silvery iron, other[b]	Electric
Hanna Furnace Corporation	Buffalo, New York	Silvery iron	Blast
Hanna Nickel Smelting Company	Riddle, Oregon	FeNi	Electric
Hooker Chemical Corporation	Columbia, Tennessee	FeP	Electric
Interlake Steel Corporation	Beverly, Ohio	FeCr, FeCrSi, FeSi, SiMn	Electric
Kawecki Chemical Company	Easton, Pennsylvania	FeCb	Aluminothermic
Mobil Chemical Company	Nichols, Florida	FeP	Electric
Molybdenum Corporation of America	Washington, Pennsylvania	FeMo, FeW, FeCb, FeB	Electric and aluminothermic
Monsanto Chemical Company	Columbia, Tennessee Soda Springs, Idaho	FeP	Electric
N L Industries, Inc.	Niagra Falls, New York	FeTi, other[b]	Electric
New Jersey Zinc Company	Palmerton, Pennsylvania	Spin	Electric
Ohio Ferro-Alloys Corporation	Brilliant, Ohio Philo, Ohio Powhatan, Ohio Tacoma, Washington	FeCr, FeSi, FeB, FeMn, SiMn, other[b]	Electric
Reading Alloys	Robesonia, Pennsylvania	FeCb, FeV	Aluminothermic
Shieldalloy Corporation	Newfield, New Jersey	FeV, FeTi, FeB, FeCb, NiCb, CrMo, other[b]	Aluminothermic
Stauffer Chemical Company	Tarpon Springs, Florida Mt. Pleasant, Tennessee Silver Bow, Montanta	FeP	Electric
Tennessee Alloys Corporation	Bridgeport, Alabama Kimball, Tennessee	FeSi	Electric
Tenn-Tex Alloy Chemical Corporation of Houston	Houston, Texas	FeMn, SiMn	Electric
Union Carbide Corporation	Alloy, West Virginia Ashtabula, Ohio Marietta, Ohio Niagra Falls, New York Portland, Oregon Sheffield, Alabama	FeB, FeCr, FeCrSi, FeCb, FeSi, FeMn, FeTi, FeW, FeV, SiMn, other[b]	Electric
U.S. Steel Corporation	Clairton, Pennsylvania McKeesport, Pennsylvania	FeMn	Blast
Woodward Iron Company	Woodward, Alabama Rockwood, Tennessee	FeSi, FeMn, SiMn	Electric

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a/ CrMo - Chromium molybdenum
FeMn - Ferromanganese
Spin - Spiegeleisen
SiMn - Silicomanganese
FeSi - Ferrosilicon
FeP - Ferrophosphorus
FeCr - Ferrochromium
FeMo - Ferromolybdenum
FeNi - Ferronickel
FeTi - Ferrotitanium
FeW - Ferrotungsten
FeV - Ferrovanadium
FeB - Ferroboron
FeCb - Ferrocolumbium
NiCb - Nickel columbium
Si - Silicon metal
FeCrSi - Ferrochromiumsilicon

b/ Includes Alsimer, Simanal, zirconium alloys, ferrosilicon, boron, aluminum silicon alloys and miscellaneous ferroalloys.

Table A-4. TOTAL FERROALLOY PRODUCTION (ALL TYPES)

Year	Production (tons)	Reference
1965	2.8×10^6	16
1969	2.6×10^6	17
1972	2.5×10^6	15

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APPENDIX B

RESULTS OF THE WRITTEN QUESTIONNAIRE

MRI developed a four-page questionnaire for use in gathering information from the seven producers of hydrogen cyanide. The questionnaire requested information on production, capacity, manufacturing and waste treatment methodologies of cyanides in all physical forms and as a constituent of any type of processed material. Copies of the questionnaire and an accompanying explanatory cover letter were sent to the corporate offices of the following companies:

- American Cyanamid Company
- Dow Chemical Company
- E. I. du Pont de Nemours and Company, Inc.
- Hercules, Inc.
- Monsanto Company
- Rohm and Haas Chemical Company
- Vistron Corporation, Division of Standard Oil of Ohio

A sample copy of the entire questionnaire, including the cover letter, follows.

Midwest Research Institute is presently conducting a program for the Office of Toxic Substances of the U.S. Environmental Protection Agency under Contract No. 68-01-2687. The primary purpose of this program is to compile information on the production, formulation, use, and treatment of inorganic cyanides and to evaluate the extent that they are released into the environment.

The following inorganic cyanides have been identified as being pertinent to this study:

HCN, hydrogen cyanide	Ferrocyanides
NaCN, sodium cyanide	Ferricyanides
KCN, potassium cyanide	heavy metal cyanides
$Ca(CN)_2$, calcium cyanide	Iron blue

The MRI study is based on information in the chemical literature and private communications with industry personnel, via telephone, letters, questionnaires and personal interviews. In order to obtain a statistically reliable overview of the industrial situation on the subject, it is important that we contact as many industries as possible. We, therefore, respectfully solicit your cooperation in completing this questionnaire; your early response (within 4 weeks) will be sincerely appreciated.

In responding to this request, we do not seek information of a proprietary nature. The results of the study will be developed in terms of industrywide practices and trends.

If your department cannot supply the requested information, please forward this questionnaire to other departments which can respond. If any questions should arise concerning this questionnaire, please contact Dr. Ralph Wilkinson at (816) 561-0202.

Please return the completed questionnaire to:

Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110

Attn: Ralph Wilkinson

Your cooperation in this matter will be appreciated.

QUESTIONNAIRE PREPARED FOR OFFICE OF TOXIC SUBSTANCES
U.S. ENVIRONMENTAL PROTECTION AGENCY

(Please fill in the details and check the appropriate blanks.)

1. Parent Corporation Name: ______________________________

   Mailing Address: ______________________________

   ____

   ____

2. Person to contact regarding information supplied in questionnaire.

   Dr/Mr/Ms: ______________________________

   Address: ______________________________

   ____

   ____

   Telephone: ______________

3. If your company manufactures, or has manufactured within the past 10 years, any of the chemicals listed in the cover letter please complete the following form:

	Listed Chemical	Production Site: City or Town and State
a.		
b.		
c.		
d.		
e.		
f.		

4. What are the sources of each cyanide-material and the approximate annual consumption?

	Cyanide-Material	Source	Approx. Annual Consumption
a.			
b.			
c.			
d.			
e.			
f.			

5. To the extent possible, within the constraints of proprietary considerations for each product or formulation identified in Item 3, please describe briefly the usage process.

Cyanide-Material	Usage Process Description (e.g., major reactions carried out or U.S. Patent Number)	Approximate Annual Process Usage

6. Has any chemical analysis ever been made on any of your by-products or waste material from the use-process(es) to determine the presence of cyanides?

In by-products? Yes ______ No ______

In process waste material? Yes ______ No ______

7. For each "yes" answer to any category in Question 6, please identify the cyandide(s) by name(s) and form(s) (i.e., solid, liquid or gas). Also, please indicate the plant location(s) for each.*

Compound(s)	Form(s)	Plant Location(s)

* If additional space is required, please use the back of this sheet.

8. For each cyanide-material listed in Question 7, please indicate the approximate concentration level of each compound(s) prior to and after waste chemical treatment and where the material appears (i.e., by-product, or process waste material). If any compound appears in two or more instances, please distinguish between the entries.

Compound(s)	Where Material Occurs	Concentration Level Prior to Treatment	Concentration Level After Treatment

9. Please provide a chronological description of your cyanide waste disposal and treatment facilities during the last 10 years. This should include liquid effluents, solid wastes and, if applicable, contract disposal services.

A discussion and summary of the replies to this written inquiry are presented in the following paragraphs.

1. American Cyanamid Company: Hydrogen cyanide and sodium ferrocyanide are produced at South Kenner, Louisiana. Hydrogen cyanide was produced by the Andrussow process from 1954 to 1966. After 1966, hydrogen cyanide was obtained as by-product from the SOHIO-acrylonitrile process. Ferrocyanide has been produced since 1971 by reaction of sodium cyanide and ferrous chloride. Plant capacity was not given. Current annual production of hydrogen cyanide is 22 million pounds and that of sodium ferrocyanide is 10 million pounds. Both products are for captive consumption.

Wastes include hydrogen cyanide in vent gases, salts of hydrogen cyanide, metal cyanide complexes and organic cyanides (cyanohydrins) as solutions or solids.

Waste treatment and handling methodologies include alkaline chlorination in a recycle lagoon system, incineration, and an increasing reliance on disposal wells.

A second cyanide facility that American Cyanamid operates is located at Willow Island, West Virginia, where iron blue has been manufactured since 1964. Iron blue is prepared by combining sodium ferrocyanide, ferrous sulfate, and ammonium sulfate under oxidizing conditions. Plant capacity was not given. Production of iron blue averaged 8 million pounds annually over the last 10 years.

The previous comments on cyanide wastes and treatment methodologies also apply in the West Virginia location.

2. Dow Chemical Company: Hydrogen cyanide has been manufactured at Freeport, Texas, since 1958 by the Andrussow process and is captively consumed. Current capacity and production data were not given.

According to Dow Chemical Company, the hydrogen cyanide is produced as a transitory intermediate and is present for only a few seconds. It is neither processed, purified, nor sold. The primary use of hydrogen cyanide appears to be in the synthesis of chelating agents, e.g., NTA and EDTA.

No detailed discussion of cyanide wastes nor treatment methodologies was given. In-process control results in an effluent that contains < 0.2 mg/liter cyanide.

3. **E. I. du Pont de Nemours and Company, Inc.**: Hydrogen cyanide has been manufactured by the Andrussow process at Memphis, Tennessee, since 1952. The material is used captively for the production of acetone cyanohydrin and liquid HCN is available for merchant sales. Other primary and captive production facilities are located at LaPlace, Louisiana, and Victoria, Texas, but details are lacking. Adiponitrile synthesis appears to be the major use of hydrogen cyanide at these two locations.

Hydrogen cyanide has also been manufactured as by-product from acrylonitrile at Beaumont, Texas, since 1970 and at Memphis, Tennessee. Again, details are lacking as to capacity and production levels. Hydrogen cyanide is used to manufacture butyronitrile derivatives at the Beaumont facility and sodium and potassium cyanide at the Memphis facility.

Waste cyanides occur in all manufacturing operations, principally as rinse waters, gases and solutions. Various waste treatment techniques reduce the cyanide level to < 0.2 mg/liter.

Liquid waste treatment methodologies include:

* Alkaline chlorination (1952 to date).

* Incineration, including flaring for gaseous effluents (1966 to date).

* Barging to the Gulf of Mexico (1969 to 1970).

* Alkaline hydrolysis (Kastone process) (1973 to date).

Solid waste treatment methdologies include:

* Landfill on site (some of the waste receives alkaline hydrolysis prior to land fill operation) (1955 to date).

* Burial of spent radioactive catalyst containing trace cyanide residues at approved Atomic Energy Commission site (1968 to 1973).

Du Pont also has facility at Niagara Falls, New York, where heavy metal cyanides have been manufactured since 1912. The cyanides include those of copper, zinc, and double-salts as sodium-copper cyanide and potassium-copper cyanide. Capacity and production data are lacking. These materials are generally made by simple replacement reactions involving sodium or potassium cyanide and the appropriate metal salt as chloride or sulfate.

Wastes include solutions containing traces of soluble cyanides and cyanogen gas. Some solid zinc cyanide may occur as waste material.

Cyanide wastes are currently and have historically been mixed in the plant process sanitary sewer with large excesses of calcium hypochlorite before discharge to the City of Niagara Falls Treatment Plant. The Du Pont plant anticipates operation of a pretreatment facility to handle all plant wastes by December 1976. When operational, the concentration of oxidizable cyanide in the total plant waste will be < 0.1 mg/liter prior to release to the City of Niagara Waste Treatment Plant.

4. Monsanto Company: Hydrogen cyanide is produced captively at Texas City (primary) and Alvin, Texas (by-product). Both the Andrussow and acrylonitrile processes are operational. The hydrogen cyanide is produced for the manufacture of NTA, t-butylamine, and lactonitrile. Capacity and production levels of all of these chemicals are lacking.

Hydrogen cyanide appears in waste streams, and after chlorination, the cyanide level is reduced to < 0.1 mg/liter.

Waste treatment methodologies include alkaline chlorination with chlorine gas (until 1974) and more recently, alkaline chlorination using a sodium hypochlorite generator.

5. Vistron Corporation: Hydrogen cyanide has been produced for merchant sales as by-product from the SOHIO-acrylonitrile process at Lima, Ohio, since 1962. Annual production is about 29 million pounds.

Hydrogen cyanide, ferro-ferricyanides, and cyanohydrins are present in waste gases and process water. Cyanide waste levels in process effluents are < 0.02 mg/liter after treatment and before release to a nearby river. Some liquid wastes are handled by deep well injection and bio-oxidation systems. Gaseous effluents containing hydrogen cyanide are incinerated.

Hercules, Inc., of Glens Falls, New York, and Rohm and Haas of Deer Park, Texas, declined to participate in the written questionnaire. Each stated that technical and manufacturing information regarding hydrogen cyanide and other cyanides had been released to the appropriate EPA Regional Offices.